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EE/CA and RI/FS Support Sampling Plan

Sauget Area 1

Sauget and Cahokia, Illinois

Volume 2 - Appendix A

Analytical Laboratory

Standard Operating Procedures

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Submitted To:

U.S. Environmental Protection Agency
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Submitted By:

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ORTHOPHOSPHATE: MANUAL COLORIMETRIC

1.0 SCOPE AND APPLICATION

This procedure describes the determination of orthophosphate in a variety of matrices including groundwater, drinking water, surface and domestic waters, industrial wastes, and soils leachates. The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are listed in Section 5 of the current revisions of the Savannah Laboratories' quality assurance plans.

2.0 SUMMARY OF METHOD

Orthophosphate reacts with molybdate and antimony ions contained in a proprietary reagent from Hach which produces a phospho-molybdenum-antimony complex. The resulting blue color is measured at 660 nm. This method is based on the guidance in EPA Methods 365.2 and 365.3.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst must wear a lab coat or apron, eye protection, and gloves when handling the samples and reagents. The analyst must also be familiar with the Material Safety Data Sheets (MSDS) for each standard and reagent. The MSDS list the type of hazard that each material poses and provide guidance for safely handling these materials.

4.0 INTERFERENCES

Blue colored components may interfere. High concentrations of arsenic may interfere.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous samples are collected in 120-mL plastic bottles and are either unpreserved or preserved with sulfuric acid. The samples are iced at the time of collection and stored at 4°C (less than 6C with no frozen samples) until the time of analysis. The holding time for orthophosphate in liquids is 48 hours.

Soil samples are collected in plastic or glass jars. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen sample) until the time of preparation and analysis. The hold time for soil samples is 28 days from collection.

6.0 APPARATUS AND MATERIALS

6.1 Spectrometer with 1cm cells

6.2 Syringes, 10 cc

6.3 Filters, 20-um

6.4 Volumetric flasks: 1000-, 100-, 10-mL

6.5 Pipettes: 1.0-, 0.5-, 0.1-, 0.05-mL

6.6 Disposable plastic cups or other suitable containers

7.0 REAGENTS

The preparation of reagent s must be tracked in accordance with SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-lab-generated deionized water

7.2 Hach phosphate powder pillows

8.0 STANDARDS

The preparation of standards must be tracked in accordance with SL SOP AN41: *Standard Material Traceability.*

8.1 Phosphate stock standard: 50 mg/L, commercially available.

8.2 Intermediate Standard (5.0mg/L) : Dilute 2.5 mL of the 50mg/L stock to 25mL with reagent water.

8.3 Calibration Standards

CAL STD	Int Conc (mg/L)	mL intermediate	final volume mL	Conc cal std (mg/L)
1	5.0	0.50	50	0.050
2	5.0	1.0	50	0.10
3	5.0	2.5	50	0.25
4	5.0	5.0	50	0.50
5	5.0	10	50	1.0

8.4 Verification Standard
A second source or PE sample may be used to verify the initial calibration. The concentration of the verification standard should be in the mid range of the calibration curve (0.2-0.5mg/L).

9.0 SAMPLE PREPARATION

9.1 Aqueous samples are analyzed directly as given below. If a sample contains high levels of suspended material or is highly colored, the sample may require filtration prior to analysis.

MS/MSD are analyzed at a frequency of 10% of samples. The matrix spikes for liquid samples are prepared by adding 0.10mL of the 50mg/L stock to 25 ml of sample. The theoretical concentration is calculated:

$$Cms(mg/L) = \frac{0.10mL \otimes 50mg/L}{0.025L} = \frac{0.00010L \otimes 50mg/L}{0.025L} = 0.20mg/L$$

The LCS for liquid samples is the initial calibration verification standard (ICV) (see Section 8.4).

9.2 Solid samples

9.2.1 Weigh out approximately 5g (5-5.5g) into a 100-mL screw-cap plastic bottle. Record the weight to the nearest 0.1g.

Prepare a method blank by adding 100mL of reagent water to an extraction bottle. Assume a sample weight of 5.0g

Prepare an LCS by adding 0.5mL of the 50mg/L stock to 100mL of reagent water in an extraction bottle. Assume a sample weight of 5.0g.

$$Clcs(mg/kg, dw) = \frac{0.50mL \otimes 50mg/L}{0.0050kg} = \frac{0.00050L \otimes 50mg/L}{0.0050kg} = 5.0mg/kg$$

Weigh two additional 5g aliquots of one of the samples for the MS and MSD. Add 0.5mL of the 50mg/L stock. The theoretical concentration of the MS/MSD is:

$$Cms(mg/kg, dw) = \frac{0.50mL \otimes 50mg/L}{W \otimes solids} = \frac{0.00050L \otimes 50mg/L}{W \otimes solids} = \frac{0.025mg}{W \otimes solids}$$

W = weight of sample extracted
solids = (percent solids)/100

9.2.3 Add 100 mL of DI water to each container (except blank and LCS) and place on the extractor. Rotate for 24 hours.

9.2.4 Remove the containers from the extractor and allow the leachates to settle. Filter the extract using a syringe filter with a 0.20-um pore size filter and analyze the extracts as liquid samples.

10.0 ANALYTICAL PROCEDURE

10.1 Remove the samples from the storage refrigerator and allow the samples to come to room temperature prior to analysis. Prepare the calibration standards and spiking solution while the samples are equilibrating.

10.2 Pour 25mL of each sample or leachate, calibration standard, or QC item into labeled containers.

10.3 Add a Hach phosphate powder pillow to each calibration standard, sample, and QC item. Allow the color to develop for 10 minutes.

10.4 Read and record the absorbance at 660nm.

ANALYTICAL SEQUENCE

Initial Calibration
Initial Calibration Verification (ICV)
Calibration blank (ICB)
10 Sample analyses
Continuing calibration verification (CCV)
Calibration blank (CCB)
10 Sample analyses
Continuing calibration verification (CCV)
Calibration blank (CCB)

10.5 Evaluate the calibration curve with a calculator or spreadsheet capable of linear regression. If the correlation coefficient is greater than 0.995, the curve can be used to quantitate samples. If less than 0.995, prepare a new curve and reevaluate.

10.6 Determine the concentration of each sample from the regression curve. If the concentration of any sample exceeds the highest concentration in the calibration curve, reanalyze a more dilute aliquot of that sample.

Sample Aliquot (mL)	Final Volume (mL)	Dilution Factor
1.0	25	25
2.5	25	10
5.0	25	5.0
12.5	25	2.0
0.50	25	50
0.25	25	100

11.0 CALCULATIONS

11.1 Liquids

$$Concentration(mg / L) = Ccurve \otimes DF$$

where

Ccurve = concentration form regression curve (mg/L)
DF = dilution factor

11.2 Soils

$$Concentration(mg / kg, dw) = Ccurve \otimes DF \otimes \frac{F}{W \otimes solids}$$

where

Ccurve = concentration form regression curve (mg/L)
DF = dilution factor
F = final volume of the extract (L)
W =weight of sample extracted (kg)
solids = (percent solids)/100

12.0 QUALITY CONTROL/QUALITY ASSURANCE

Evaluate the QC in accordance with SL SOP AN02: *Analytical Batching.*

13.0 PREVENTIVE MAINTENANCE-none

14.0 TROUBLE-SHOOTING-none

15.0 REFERENCES

Methods for Chemical Analysis of Water and Wastes; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983.

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FLUORIDE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of fluoride in drinking water, surface water, saline water, domestic and industrial wastewater, and in soils and sediments.

1.2 The Reporting Limit (RL) for fluoride in liquid samples is 0.020 mg/L, and the RL for fluoride in soils/sediments is 4.0 mg/kg for a 5-g sample (assuming 100% solids).

2.0 SUMMARY OF METHOD

2.1 Liquid samples are buffered, and the fluoride is measured potentiometrically using a combination fluoride selective electrode.

2.2 A 5-g soil sample is mixed with 100 mL of reagent water and extracted for 2 hours on a rotary extractor. The soil/water mixture is allowed to settle and the supernatant is decanted, buffered, and the fluoride is measured in the decanted liquid. The fluoride is measured potentiometrically using a combination fluoride selective electrode.

2.3 This method is based on EPA Method 340.2(1).

3.0 SAFETY

3.1 **Under no circumstances are samples to be distilled prior to analysis.** The distillation procedure involves the use of concentrated sulfuric acid at temperatures that approach the boiling point of sulfuric acid.

NOTE: The Sixteenth Edition of *Standard Methods* states:

> "Adding the prescribed buffer frees the electrode from most interferences that adversely affect the SPADNS colorimetric method and necessitate preliminary distillation."(2)

3.2 The standards and reagents used in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.3 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses, the safe handling instructions for these compounds, and first aid instructions.

4.0 INTERFERENCES

4.1 Extreme sample pH will interfere with the operation of he fluoride electrode. The sample pH should be between 5 and 9. The addition of the buffer solution will bring most samples into the optimal range.

4.2 The following cations can interfere with the measurement of fluoride by complexing with fluoride: Si^{4+}, Fe^{3+}, and Al^{3+}. The buffer solution contains a chelating agent that will eliminate the interference caused by these cations.

NOTE: The Sixteenth Edition of *Standard Methods* states:

> "Adding the prescribed buffer frees the electrode from most interferences that adversely affect the SPADNS colorimetric method and necessitate preliminary distillation."(2)

4.3 Sulfate at very high concentrations (> 50000 mg/L) can be a negative interference and alkalinity at very high concentrations (> 7000 mg/L) can be a positive interference.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Soil samples are collected in wide-mouth glass or plastic jars. No preservative is added to the sample. The holding time is 28 days.

5.2 Liquid samples are collected in 250-mL plastic bottles. No preservative is added to the sample. An orange dot is affixed to the outside of the container to show that no preservative has been added to the container. The holding time is 28 days.

6.0 APPARATUS AND MATERIALS

6.1 Electrode meter with expanded millivolt scale
6.2 Combination fluoride selective electrode
6.3 Magnetic stirrer with Teflon-coated stir bars
6.4 Disposable cups

7.0 REAGENTS

7.1 Reagent water - lab generated deionized water

7.2 Glacial acetic acid - reagent grade

7.3 Sodium Chloride - reagent grade

7.4 CDTA (1,2-cyclohexylene dinitrilotetraacetic acid, monohydrate) - reagent grade

7.5 Sodium hydroxide - reagent grade

7.6 Sodium hydroxide (5N): Measure 600 mL of reagent water into a 1-L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Weigh out 200 g of sodium hydroxide into a 400-mL beaker. Add a small quantity of the sodium hydroxide from the beaker to the reagent water in the beaker on the magnetic stir plate. As the sodium hydroxide dissolves, add more of the sodium hydroxide from the beaker until all 200 g has been added. Dilute the solution to a volume of 1.0 L with reagent water. Transfer the reagent to a 1-L bottle. Do not store reagents in volumetric glassware. Prepare this reagent monthly. Label the reagent bottle with the reagent name,analysis, concentration, batch ID, date prepared, expiration date, and the analyst's initials. Record the reagent preparation information in the reagent preparation log. (Figure 2)

CAUTION: Heat will be evolved as the sodium hydroxide dissolves in the water. This solution is caustic and will cause skin burns and destroy unprotected clothing.

7.5 Buffer solution (pH 5.0 - 5.5): Add about 1 L of reagent water to a 2-L beaker. Add 114 mL of glacial acetic acid, 116 g of sodium chloride, and 4 g of CDTA. Stir the solution to dissolve the solid reagents. Cool the solution to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5N sodium hydroxide. Approximately 300 mL of the 5N NaOH will be required. Prepare this solution monthly. Label the reagent bottle with the reagent name, analysis, concentration, batch ID, date prepared, expiration date, and the analyst's initials. Record the reagent preparation information in the reagent preparation log. (Figure 2)

7.6 Hydrochloric acid (HCl) - reagent

7.7 Hydrochloric acid (1N): Add 500 mL of reagent water to a 1-L volumetric flask. Carefully add 83.4 mL of concentrated HCl to the volumetric flask. Dilute to volume with reagent water. Prepare this solution monthly. Label the reagent bottle with the reagent name, analysis, concentration, batch ID, date prepared,expiration date,and the analyst's initials. Record the reagent preparation information in the reagent preparation log. (Figure 2)

8. STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis of purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with SL SOP AN41: *Standard Material Traceability in Inorganic Analyses.*

8.1 Preparation of the Calibration Standards

8.1.1 Ammonium fluoride (NH_4F) - reagent grade

8.1.2 Fluoride stock standard (100 mg/L): Dissolve 0.1947 g of NH_4F in some reagent water in a 1-L volumetric flask. Dilute to volume with reagent water. Transfer the stock standard to a polypropylene bottle and store in the refrigerator at 4° C ± 2° C. Prepare fresh monthly. Label the standard with the standard name, concentration, batch ID, date prepared, expiration date, and analyst's initials. Record the standard reparation information in the stock standard preparation log.

8.1.3 The working calibration standards are prepared from the fluorine stock standard (100 mg/L).

8.1.3.1 For each working calibration standard to be prepared, measure 50 mL of reagent water into a plastic cup. In this method, seven working calibration standards and a calibration blank are prepared and analyzed.

8.1.3.2 Using a calibrated volumetric pipet, remove the volume of dilution solution that corresponds to the volume of fluorine stock standard (100 mg/L) that is to be added to make the working calibration solution. Using a calibrated volumetric pipet, replace the volume of the dilution solution that was removed with corresponding volume of the fluorine stock (100 mg/L).

For example, to prepare the 1.0 mg/L working calibration standard, remove 0.50 mL of the dilution solution from the plastic cup and pipet 0.50 mL of the fluorine stock standard (100 mg/L) into the plastic cup. The final volume is 50 mL. The following table gives guidance for the preparation of the seven working calibration standards and the calibration blank:

Working Calibration Standard (mg/L)	Volume of 100 mg/L Fluorine Stock Standard (mL)	Final Volume (mL)
0.10	0.050	50
0.30	0.15	50
1.0	0.50	50
2.0	1.0	50
3.0	1.5	50
10	5.0	50
20	10	50
calibration blank	0	50

8.1.3.3 Record the working standard information into the preparation log. (Figure 3)

8.2 Preparation of the matrix spike solution

The matrix spiking solution is the 100-mg/L fluorine stock standard. A known volume of the fluorine standard is added to a known volume of a liquid sample or to a 5-g aliquot of a soil sample mixed with 100 mL of reagent water.

8.2.1 Liquid samples: Using a calibrated pipet, transfer 0.50 mL of the 100-mg/L fluorine stock standard to a 50-mL aliquot of sample (or to a volume diluted to 50 mL). The concentration of the matrix spike sample is given as follows:

$$mg/L = \frac{100\ mg/L \otimes 0.5\ mL}{50\ mL} = \frac{100\ mg/L \otimes 0.0005\ L}{0.050\ L} = 1.0\ mg/L$$

8.2.2 Soil/solid samples: Using a calibrated pipet, transfer 1.0 mL of the 100-mL fluorine stock standard to a 5-g aliquot of sample mixed with 100 mL of reagent water. The concentration of the matrix spike sample is given as follows:

$$mg/L = \frac{100\ mg/L \otimes 1.0\ mL}{(5\ g)(solids)} = \frac{100\ mg/L \otimes 0.001\ L}{(o.005\ kg)(solids)} = 20\ mg/kg, if\ solids = 1.0$$

Solids is the decimal equivalent of the % solids and is calculated as:

$$Solids = \frac{percent\ solids}{100}$$

For example, if the percent solids is 85%, the decimal equivalent is 0.85; if the % solids is 100%, the decimal equivalent is 1.0.

8.3 Lab Control Standards

The lab control standard is purchased from ERA (Environmental Resource Associates). The standard comes in a vial that is diluted to a specified volume with reagent water. The lab control standard (LCS) is distilled and analyzed. The results are compared to the values contained on the certificate of analysis.

9.0 SAMPLE PREPARATION

9.1 Liquid samples are analyzed as received.

NOTE: For each batch of 20 or fewer samples, a method blank, a lab control standard, a lab control standard duplicate, a matrix spike and a matrix spike duplicate (if there is sufficient sample for the MS/MSD) must be analyzed.

9.2 Soil Samples

9.2.1 A 5-g aliquot of the soil sample (weighed to the nearest 0.1 g) is added to a 120-mL plastic bottle.

9.2.2 Add 100 mL of reagent water to the bottle. The bottle is capped and placed on a rotary extractor and extracted for 2 hours.

9.2.3 After the extraction is completed, the sample is removed from the extractor and allowed to settle.

9.2.4 Decant 50 mL of the supernatant and place the supernatant in a plastic cup. The sample extract is ready for the determination of fluoride.

NOTE: For each batch of 20 or fewer samples, a method blank, a lab control standard, a lab control standard duplicate, a matrix spike and a matrix spike duplicate (if there is sufficient sample for the MS/MSD) must be extracted and analyzed.

10. PROCEDURE

10.1 Initial Calibration

10.1.1 Prepare the initial calibration standards. (Section 8.1)

10.1.2 Add 50 mL of the CDTA buffer (7.5) to each calibration standard.

10.1.3 Add a stir bar to the cup, place the cup on a magnetic stirrer, and mix at medium speed.

10.1.4 Lower the electrode into the liquid. The electrode must remain in the sample for at least three minutes and until the millivolt reading has stabilized. For fluoride concentrations < 0.5 mg/L, the electrode may take longer to stabilize. Rinse the electrode with reagent water and blot the electrode dry with a Kimwipe between readings.

10.1.5 Record the potential reading for each standard on the appropriate log sheet. (Figure 4)

10.1.6 The calibration curve is plotted on semilog paper. The concentrations are plotted on the log scale and the potential readings are plotted on the linear axis.

Alternatively, the logarithm of the concentration and the corresponding potential are entered into a calculator or PC capable of linear regression. The log of the concentration is entered as the x-axis value and the corresponding potential is entered as the y-axis value. The correlation coefficient must be greater than 0.995. If the correlation coefficient is less than 0.995, contact the immediate supervisor to determine the cause of the problem. If the problem cannot be identified and corrected, new calibration standards are prepared, analyzed, and evaluated.

10.2 Sample Analysis

After the analysis and evaluation of the initial calibration standards, the measurement of fluoride in the samples can begin.

10.2.1 For the analysis of liquid samples, measure 50 mL of liquid sample (or an aliquot of sample diluted to 50 mL) into a plastic cup. For the analysis of soil sample extracts, measure 50 mL of the soil reagent water extract (or an aliquot of the reagent water extract diluted to 50 mL) into a plastic cup.

10.2.2 Add 50 mL of CDTA buffer to each sample, method blank, and QC sample. Check the pH of the sample with pH paper prior to measurement of fluoride. Extreme sample pH will interfere with the operation of the fluoride electrode. The sample pH should be between 5 and 9. The addition of the buffer solution will bring most samples into the optimal range. If the pH is greater than 9, adjust the pH to the 5 to 9 range with 1N HCl (7.7).

10.2.3 Add a stir bar to the cup, place the cup on a magnetic stirrer, and mix at medium speed.

10.2.4 Lower the electrode into the liquid. The electrode must remain in the sample for at least three minutes and until the millivolt reading has stabilized. For fluoride concentrations < 0.5 mg/L, the electrode may take longer to stabilize. Rinse the electrode with reagent water and blot the electrode dry with a Kimwipe between readings.
10.2.5 Record the potential reading for each standard on the appropriate log sheet. (Figure 4)

The samples are analyzed in the following sequence:

Initial Calibration Standards
Initial Calibration Verification (ICV) - LCS or LCSD
Initial Calibration Blank (ICB) - calibration blank
10 Sample Readings (including method blank, MS/MSD)
Continuing Calibration Verification (CCV) - LCS or LCSD
Continuing Calibration Blank (CCB) - calibration blank
10 Sample Readings (including method blank, MS/MSD)
CCV - LCS or LCSD
CCB - calibration blank
10 Sample Readings (including method blank, MS/MSD)
CCV - LCS or LCSD
CCB - calibration blank

10.11.1 The Initial Calibration Verification (ICV) is analyzed immediately after the calibration curve criteria is met. The ICV is either the LCS of LCSD that has been taken through the entire analytical process. The ICV is used to verify that the calibration curve has been properly constructed. The recovery of the ICV must be between 75% and 125%.

10.11.2 The Initial Calibration Blank (ICB) is analyzed after the ICV. The ICB is the calibration blank that contains all of the reagents that have been added to the calibration standards. The ICB is not extracted (soils). The ICB serves as a check on contamination due to the reagents. The concentration of fluoride in the ICB must be less than 0.20 mg/L.

10.11.3 After the ICV and ICB criteria has been met, ten sample potentiometric readings may be taken. The method blank should be analyzed early in the sequence as a check for contamination in the extraction (soils) and analytical process.

10.11.4 If the concentration of a sample exceeds the linear range of the calibration curve, a smaller volume of distillate is diluted to 50 mL and reanalyzed.

10.11.5 After ten potentiometric readings, the Continuing Calibration Verification (CCV) is analyzed. The CCV is either the LCS or LCSD that has been taken through the entire extraction (soils) and analysis process. The recovery of the CCV must be between 75% and 125%.

10.11.6 After the CCV criteria is met, the Continuing Calibration Blank (CCB) is analyzed. The CCB is the calibration blank (same as ICB) and serves as a continuing check on contamination due to reagents.

The concentration of fluoride in the CCB must be less than 0.20 mg/L.

10.11.7 After the CCV and CCB criteria is met, ten sample potentiometric readings can be taken. The sequence (10.11) continues until the CCV/CCB criteria fails or until all samples are analyzed. The sequence is capped with the analysis of the CCV and CCB.

11. DATA ANALYSIS/CALCULATIONS

11.1 The concentrations of fluoride in client and QC samples are taken from the calibration curve or from the linear regression curve. The concentration may be determined directly from the calibration curve or from the x-intercept determination from the calculator or PC using linear regression. ***If the calculator is used,remember to take the inverse log of the sample concentrations to provide the concentration in the correct units.***

11.1.1 The results for liquid samples is calculated as follows:

$$mg/L\,(in\ sample) = mg/L\,(from\ curve) \otimes DF$$

where

DF = dilution factor (10.2.6)

EXAMPLE CALCULATIONS

Fifty (50) mL of the sample is analyzed and the concentration is determined to be 0.25 mg/L. The concentration of fluoride in the sample is:

$$mg/L = 2.5\,mg/L \otimes 10 = 25\,mg/L \quad (dilution\ factor = 50/5 = 10)$$

Five (5.0) mL of a liquid sample is diluted to 50 mL. The concentration in the diluted sample is found to be 2.5 mg/L. The concentration of fluoride in the sample is:

$$mg/L = 2.5\,mg/L \otimes 10 = 25\,mg/L \quad (dilution\ factor = 50/5 = 10)$$

The Reporting Limit (RL) is calculated:

$$RL\,(mg/L) = 0.20\,mg/L \otimes DF$$

where

0.20 mg/L is the SL Quality Assurance Plan Reporting Limit and assumes that 50 mL of sample is analyzed (DF = 50/50 = 1)

11.1.2 The results for soil sample are calculated as follows:

$$mg/kg\,(dwb) = mg/L\,(from\ curve) \otimes \frac{0.10\,L}{Wd} \otimes DF \otimes \frac{1}{solids}$$

where

Wd = weight of sample extracted (kg) (1 g = 0.001 kg)
dwb = dry weight basis
DF = dilution factor (10.6)

Solids is the decimal equivalent of the % solids and is calculated as:

$$solids = \frac{percent\ solids}{100}$$

For example, if the percent solids is 85%, the decimal equivalent is 0.85; if the % solids is 100%, the decimal equivalent is 1.0.

EXAMPLE CALCULATIONS

Greater than 5.0 g of a soil sample that is 100% solids is extracted with 100 mL of reagent water, and 50 mL of the extract is analyzed. The concentration of fluoride in the extract is determined to be 2.0 mg/L.

The concentration of fluoride in the soil sample is:

$$mg/kg\,(dwb) = 2.0\,mg/L \otimes \frac{0.10\,L}{0.005\,kg} \otimes 1 \frac{1}{0.25} = 40\,mg/kg\,(dwb)$$

(Recall that 5.0 G = 0.0050 kg)
DF = 50/50 = 1

Greater than 5.5 g of a soil sample that is 25% solids is extracted with 100 mL of reagent water. Twenty (20) mL of the extract is diluted to 50 mL with reagent water and analyzed. The concentration in the diluted extract is determined to be 5.6 mg/L. The concentration of fluoride in the sample is calculated as follows:

$$mg/kg\,(dwb) = 5.6\,mg/L \otimes \frac{0.10\,L}{0.0055\,kg} \otimes 2.5 \otimes \frac{1}{0.25} = 1018\,mg/kg\,(dwb)$$

(Recall that 5.5 g = 0.0055 kg)
Dilution factor = 50/20 = 2.5
This result would be reported at 1000 mg/kg (dwb)

The Reporting Limit (RL) is calculated:

$$mg/kg\,(dwb) = 4.0\,mg/kg \otimes \frac{0.10\,kg}{Wd} \otimes DF \otimes \frac{1}{solids}$$

where

Wd = weight of sample extracted (kg)
4.0 mg/kg is the SL Quality Assurance Plan Reporting Limit, and assumes that 5 g of sample is extracted, that the sample is 100% solid, and that 50 mL is the extract is analyzed (the DF = 1).

Solids is the decimal equivalent of the % solids and is calculated as:

$$solids = \frac{percent\ solids}{100}$$

For example, if the percent solids is 85%, the decimal equivalent is 0.85; if the % solids is 100%, the decimal equivalent is 1.0.

11.2 The concentration of fluoride in the lab control and matrix spike samples is determined as in Section 11.1. The concentration is compared to the theoretical spike concentration and the percent recovery is calculated.

11.2.1 A liquid sample matrix spike is prepared by adding 0.50 mL of the 100-mg/L fluoride stock solution to a 50-mL aliquot of a liquid sample. A soil/solid sample matrix spike sample is prepared by adding 1.0 mL of the 100 mg/L fluoride stock standard to 5.0 g of a soil sample. (The soil sample is mixed with 100 mL of reagent water.)

11.2.1.1 The theoretical concentration of a liquid sample that has been spiked with the 100-mg/L fluoride stock standard is:

$$mg/kg\,(dwb) = \frac{0.50\,mL \otimes 100\,mg/L}{50\,mL} = \frac{0.0005\,L \otimes 100\,mg/L}{0.050\,L} = 1.0\,mg/L$$

11.2.1.2 The theoretical concentration of a soil sample that has been spiked with the matrix spike solution is:

$$mg/kg\,(dwb) = \frac{1.0\,mL \otimes 100\,mg/L}{5.0\,g} \otimes \frac{1}{solids} = \frac{0.0010\,L \otimes 100\,mg/L}{0.005\,kg} \otimes \frac{1}{solids}$$

$$= 20\,mg/kg\ (if\ \%\ solids = 100\%;\ that\ is\ solids = 1.0)$$

11.2.1.3 The percent recovery of the fluoride in the matrix spike sample is calculated:

$$\%\ recovery(\%\ REC) = \frac{C_{ms} - C_s}{T_s} \otimes 100$$

where

C_{ms} = concentration of the spiked sample (MS or MSD)
C_s= concentration of the unspiked sample
T_s= theoretical concentration of the spike

11.2.1.4 The matrix spike samples are analyzed in duplicate. The relative percent recovery (% RPD), a measure of precision, is calculated for the MS/MSD) pair as follows:

$$\%\ RPD = \frac{\%\ REC\,(MS) - \%\ REC\,(MSD)}{(\%\ REC\,(MS) + (\%\ REC\,(MSD))/2}$$

The absolute value of the % RPD is reported, that is, only positive values are reported.

11.2.2 The lab control standard is purchased from ERA (Environmental Resource Associates). The standard comes in a vial that is diluted to a specified volume with reagent water. The lab control standards (LCS and LCSD) are distilled and analyzed. The results are compared to the values contained on the certificate of analysis.

11.2.2.1 The recovery of the lab control standard is calculated as follows:

$$\%\ REC = \frac{C_{lcs}}{C_t} \otimes 100$$

where

C_{lcs} = concentration of the LCS or LCSD
C_t = theoretical concentration of the LCS or LCSD

The recovery of the lab control standards must be between 75% and 125%.

11.2.2.2 The lab control standards samples are analyzed in duplicate. The relative percent recovery (% RPD), a measure of precision, is calculated for the LCS/LCSD pair as follows:

$$\%\ RPD = \frac{(\%\ REC\,(LCS) - \%\ REC\,(LCS))}{(\%\ REC\,(LCS) + \%\ REC\,(LCS)/2)} \otimes 100$$

The absolute value of the % RPD is reported; that is, only positive values are reported.

The %RPD of the LCS/LCSD must be less than 20%.

12. QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to 20 client samples and the associated QC items that are extracted (soils) and analyzed together. The QC items for an analytical batch consist of a method blank, a lab control standard (LCS), a lab control standard duplicate (LCSD), a matrix spike (MS), and a matrix spike duplicate (if there is sufficient volume to perform the MS/MSD).

12.2. Evaluation of QC Data

12.2.1. The **method blank** is reagent water that is taken through all extraction and analytical procedures. The concentration of fluoride in the method blank is a measure of the contamination due to the entire extraction (soils) and analytical process.

12.2.1.1 The concentration of fluoride in the method blank must be less than 0.20 mg/L for liquids and 1.0 mg/kg for soils (assuming a "soil" weight of 5 g and 100% solids).

12.2.1.2 If the concentration of fluoride in the method blank is greater than 0.20 mg/L for liquids and 1.0 mg/kg for soils, contact the immediate supervisor to determine the cause of the contamination. If the cause of the contamination cannot be determined and corrected, the batch of samples processed with the method blank must be extracted (soils) and analyzed again.

12.2.2 The **lab control standard (LCS or LCSD)** is a standard obtained or prepared from a separate source (a source different from the source of the calibration standards) and taken through all analytical procedures. The LCS for total recoverable phenolics is purchased from ERA. A certificate of analysis must accompany the lab control standard and the certificate must be kept as a record of the true (theoretical) concentration of the LCS.

12.2.2.1 The recoveries (% REC) of the LCS and LCSD must be between 75% and 125%. The relative percent difference (% RPD) between the LCS and LCSD must be less than 20%.

12.2.2.2 If the recovery of fluoride in the LCS or LCSD is outside of the 75-125% range, contact the immediate supervisor to determine the cause. If the cause of the failure of either the % REC of % RPD cannot be determined and corrected, the batch of samples processed with the LCS/LCSD must be extracted (soils) and analyzed again.

12.2.3 The **matrix spike and matrix spike duplicate (MS/MSD)** is prepared by adding a known concentration of the 100 mg/L fluoride stock standard to a known volume or weight of a client sample. The spiked samples are processed through the entire extraction (soils) and analytical procedure. The accuracy and precision results from the MS/MSD are a measure of the effect that the sample matrix has on the determination of fluoride.

12.2.3.1 The recoveries (% REC) of the MS and MSD should be between 75% and 125%. The relative percent difference (% RPD) between the MS and MSD should be less than 20%.

12.2.3.2 If the recovery of fluoride in the MS or MSD is outside of the 75-125% range, contact the immediate supervisor to determine the cause. If the % RPD of the LCS/LCSD is greater than 20%, contact the immediate supervisor to determine the cause. If the cause of the failure of either the % REC or % RPD cannot be determined and corrected and the LCS/LCSD are within the specified control limits, the cause can be attributed to matrix interference(s).

NOTE: For projects which require Florida DEP QAS criteria, matrix spike results will be utilized for laboratory control. If the matrix spikes are out of control, laboratory control standard (LCS) and method control criteria will be utilized for ultimate control of the analytical batch.

12.3 The **method detection limit (MDL)** is defined as the concentration of an analyte that can be measured with a 99% confidence that the result is greater than zero. The MDL is determined by spiking 7 to 10 10-mL aliquots of reagent water or 7-10 5-g aliquots of blank soil (a soil that has been analyzed previously and found to contain no recoverable phenolics above the RL) with a known concentration of phenol. The spiked samples are taken through the entire extraction and analytical process. The results of the analysis of the spiked samples is used to calculate the MDL. A procedure is given to eliminate outliers from the MDL calculation.

12.3.1 Prepare the spiked samples for the determination of the Method Detection Limit.

12.3.1.1 Spike ten (10) 1-L aliquots of reagent water with 0.20 mL of the phenol matrix spiking solution (10 mg/L; Section 8.2) to determine the MDL for liquid samples. The concentration of fluoride in the water sample is Y mg/kg.

12.3.1.2 Spike ten (10) aliquots of a blank soil (a soil that has been analyzed previously and found to contain no recoverable phenolics above the RL) with X mL of the fluoride spiking solution (100 mg/L; Section 8.2) to determine the MDL for soil/solid samples. The concentration of fluoride in the soil sample is Y mg/kg.

12.3.2 Distill (Section 9 - soils) and analyze (Section 10) the MDL samples. Calculate the concentration of the samples (Section 11).

12.3.3 For each matrix (liquid or soil), tabulate the results of the analysis. Calculate the average result:

$$Average = \frac{Result\ 1 + Result\ 2 + Result\ 3 + Result\ 4 + \ldots\ldots + Result\ N}{N}$$

where

N is the total number of aliquots analyzed. If all ten aliquots are used, N = 10.

12.3.4 Calculate the standard deviation of the results used to calculate the average.

12.3.5 Calculate the Method Detection Limit (MDL) as

$$MDL = (t_{0.999})\,SD$$

where

$t_{(0.999)}$ is the Student's t-value for n-1 degrees of freedom
SD is the standard deviation of the N aliquots of MDL sample analyzed.

Degree of Freedom	$t_{(0.999)}$
1	31.821
2	6.965
3	4.451
4	3.747
5	3.365
6	3.143
7	2.998
8	2.896
9	2.821
10	2.764

(t-values are from the *Chemical Engineer's Handbook*, 4th edition, Perry, Chilton, and Kirkpatrick (1963)).

EXAMPLE CALCULATION

Ten aliquots of reagent water are spiked at 0.020 mg/L, distilled, and analyzed. The results for the ten aliquots are:

Result	Concentration (mg/L)
1	0.021
2	0.018
3	0.016
4	0.022
5	0.023
6	0.019
7	0.020
8	0.015
9	0.021
10	0.024

The average is calculated as 0.0199.
The standard deviation is calculated as 0.00292.
The MDL is calculated as SD X $t_{(0.999)}$ = 0.00292 X 2.821 = 0.0082.

12.3.6 There are times when a result (or results) obtained in the determination of the MDL doesn't look like it belongs. The "outlier(s)" may cause the MDL to be much higher or lower if it is included in the MDL calculation. The following procedure gives the steps for determining if a result should be kept or rejected.

12.3.6.1 Calculate the range of the results. The range is defined as the largest value minus the smallest value in the set of results.

12.3.6.2 Calculate the difference between the suspected result and its nearest neighbor.

12.3.6.3 Divide the difference obtained in Step 12.3.6.2 by the range from Step 12.3.6.1 to obtain the rejection quotient, Q.

12.3.6.3 Consult the table of $Q_{0.90}$ values given below. If the computed value of Q is greater than the value in the table, the result can be discarded with 90% confidence that it was subject to some factor which did not operate on the other results. If the result is less than or equal to the $Q_{0.90}$ value in the table, the result should not be rejected in the calculation of the method detection limit (MDL).

Number of Observations	$Q_{0.90}$
3	0.90
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

EXAMPLE

Ten aliquots of reagent water are spiked at 0.20 mg/L, distilled, and analyzed. The results for the ten aliquots are:

Result	Concentration (mg/L)
1	0.021
2	0.018
3	0.016
4	0.022
5	0.023
6	0.019
7	0.020
8	0.015
9	0.021
10	0.024

The average is calculated as 0.0199
The standard deviation is calculated as 0.00292.
The MDL is calculated as SD X $t_{(0.999)}$ = 0.00292 X 2.821 = 0.0082.

The result 0.015 is suspected of being an outlier. The Q value is used to determine whether this result is dept or discarded.

1) The range of values is 0.024 - 0.015 = 0.009
2) The difference between 0.015 and its nearest neighbor, 0.016, is 0.016 - 0.015 =0.001.
3) The Q value if calculated as:

$$Q = \frac{0.001}{0.009} = 0.111$$

4) There are ten observations: $Q_{0.90}$ value = 0.41. Since the calculated Q is less than the table $Q_{0.90}$, the result, 0.015, should not be discarded and is included in the calculation of the MDL.

13. REFERENCES

1. *Methods for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983.

2. *Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition*; American Public Health Association: Washington, DC, 1992.

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Approval Signature:	R. Wayne Robbins
	R. Wayne Robbins
Title:	Corporate QA Manager
	Date: 5/1/98

AVAILABLE PHOSPHORUS IN SOILS

1.0 SCOPE AND APPLICATION

This method is used to estimate the concentration of available phosphorus in soils. The practical quantitation limit for this method is 2 mg/kg.

2.0 SUMMARY OF METHOD

A hydrochloric acid/ammonium fluoride solution is used to extract the acid-soluble forms of phosphorus in a soil sample. The ammonium fluoride dissolves aluminum and iron phosphates in the acidic solution.

Orthophosphate is determined in the filtered extract and the result reported as available phosphorus in soils.

This method is based on Method 24-5.1 in Methods of Soil Analysis (1).

3.0 APPARATUS AND MATERIALS

Scintillation vials
Balance
Volumetric glassware
Syringes, 10cc
Filters, 0.2 um

4.0 REAGENTS AND STANDARDS

Ammonium fluoride, 1N: Dissolve 37 g of NH_4F in DI water, and dilute to 100 mL. Store in plastic.

Hydrochloric acid, 0.5 N: Dilute 20.2 mL of concentrated HCl to 500 mL with DI water.

Extraction solution: Add 15 mL of 1.0 N NH_4F and 25 mL of 0.5 HCl to 460 mL DI water. This yields a 0.03N NH_4F and a 0.025 N HCl solution. Store in glass.

Calibration standards: Calibration standards are prepared as given in Method GE70, except that 7 mL of extraction solution is added to each 10-mL volumetric flask before diluting to volume.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Collect samples in a widemouth glass jar. Cool to 4°C.

6.0 PROCEDURE

Weigh 1 g of soil into a scintillation vial. Add 7 mL of extraction solution. Shake 1 min. and filter with a 0.2 um syringe filter into a 10 mL volumetric flask. Dilute to volume with DI water. determine the orthophosphate concentration in the filtrate by Method GE70 or by manual spectrophotometric method.

Calculate the concentration of available phosphorus as shown below.

$$\text{Available phosphorus (mg/kg)} = \frac{(\text{mg/L P})\,(0.01\ \text{L})\,(1000\text{g})}{(\text{sample wt. g})\,(1\text{kg})}$$

7.0 QUALITY CONTROL

All samples must be extracted and analyzed in duplicate.

8.0 REFERENCES

1. *Methods of Soil Analysis*, Second Edition, Part 2; Page, A.L., Ed.; American Society of Agronomy, and Soil Science Society of America: Madison, WI, 1982.

CHANGE -IN-PROGRESS ATTACHMENT **UNCONTROLLED COPY**

SOP Document No: SM07:04.05.99:0
SOP Description: Polychlorinated Biphenyl (PCBs) by GC/MS (Method 680)

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: May 7, 1999

The following revisions or additions have been made to the referenced SOP.

Changes or updates to all sections are in bold type.

2.2 This procedure is based on the guidance provided in EPA Method 680. The method has been modified to include the use of a carbon-13 labeled analogue of decachlorobiphenyl (13C12-DCB) as the surrogate in place of the labeled BHC and DDT compounds. 13C12-DCB can be subjected to the optional acid cleanup (the unlabeled analogue, decachlorobiphenyl, is routinely used in SW-846 Method 8082). Preparation procedures are also referenced for soils and biological tissues, which are not included in EPA Method 680. A window-defining mix containing the first and last eluting isomers of each level of chlorination is used as an aid to establish and verify that the SIM windows are properly set. **Due to matrix interferences routinely present in soils and biological tissues, the initial calibration criteria has been changed to 30% RSD and the continuing calibration criteria has been changed to 30% difference from the initial calibration.**

The following section is deleted from the SOP:

10.3.4 Verify the SIM "on/off" times by re-analyzing the window-defining mix by SIM prior to the initial calibration.

Changes or updates to all sections are in bold type.

10.4.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

- **Liquids:** If the %RSD of each target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples.
- **Soils and biological tissues: If the %RSD of each target compound is less than or equal to 30%, the average response factor can be used for quantitation of samples.**
- If the %RSD of the target compound **exceeds the acceptance criteria**, the curve should be evaluated for errors and one or more standards re-analyzed. Take corrective action until the %RSD of each target **meets the acceptance criteria.**

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Changes or updates to all sections are in **bold type**.

10.5.1 The percent difference or percent drift between the continuing calibration RRF and the average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$\%difference = \left| \frac{RRF - RRFavg}{RRFavg} \right| \otimes 100$$

where
RRF = relative response factor from CCV
RRFavg = average relative response factor from initial calibration curve

Liquids: If the percent difference is less than or equal to 20% for each target compound, the initial calibration is verified.

Soils and biological tissues: If the percent difference is less than or equal to 30% for each target compound, the initial calibration is verified.

APPENDIX C
680 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time(1)	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Biological	Frozen	Glass or aluminum foil	6 months	40 days

(1) Holding times are advisory - no holding times are defined in method 680.

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 20ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
Initial Calibration-minimum of five calibration standards	After Tune Check and when calibration verification standard fails acceptance criteria.	**Liquids: %RSD <= 20%** **Soils and biological tissues:** **%RSD <=30%**	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Performance Criteria	Evaluate mid level calibration standard each clock	-Mass abundance ratios of all calibration congeners within acceptance range (see Appendix B) -Baseline separation of PCB congener #87 from congeners #154 and #77 -Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241 -decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples and at the end of the analytical sequence	**Liquids: %Difference <= 20%** **Soils and biological tissues:** **%Difference <=30%**	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: April 5, 1999

Polychlorinated Biphenyls (PCBs) by GC/MS (Method 680)

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of polychlorinated biphenyls (PCBs) in groundwater, soils, sediments, wastes, and biological tissues by GC/MS. PCBs are reported by the level of chlorination: monochlorobiphenyls, dichlorobiphenyls, trichlorobiphenyls, etc., up to decachlorobiphenyl.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for each target compound is given in Section 5 of the current revisions of the Savannah Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan.*

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is spiked with a surrogate and extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS operated in the Selected Ion Monitoring Mode (SIM). Windows are established to monitor for the characteristic masses of the various PCB congeners. Qualitative identification of the target compounds in the extract is based on the presence of the peak within the SIM window and the mass ratio between the primary and confirmation ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion. Results are reported as total monochlorobiphenyls, total dichlorobiphenyls, etc.

2.2 This procedure is based on the guidance provided in EPA Method 680. The method has been modified to include the use of a carbon-13 labeled analogue of decachlorobiphenyl (13C12-DCB) as the surrogate in place of the labeled BHC and DDT compounds. 13C12-DCB can be subjected to the optional acid cleanup (the unlabeled analogue, decachlorobiphenyl, is routinely used in SW-846 Method 8082). A window-defining mix containing the first and last eluting isomers of each level of chlorination is used as an aid to establish and verify that the SIM windows are properly set. Preparation procedures are also referenced for soils and biological tissues, which are not included in EPA Method 680.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.2 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products such as diesel or waste oil. GPC cleanup may be necessary for biological tissues.
Acid cleanup may be employed as an additional cleanup tool.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Container	Sample Hold Time[1]	Extract Hold Time[1]
Aqueous	none; 4C +/- 2C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C +/- 2C	500-mL	14 days	40 days
Biological	Frozen	Glass or wrapped in aluminum foil	6 months	40 days

[1] Holding times are advisory - no holding times are defined in method 680.

6.0 APPARATUS AND MATERIALS

6.1 GC/MS System with compatible data system autosampler, splitless injector, and direct capillary interface.

6.2 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID, 0.25um film thickness. Equivalent columns can be used.

6.3 Microsyringes-

6.4 Volumetric flasks, Class A-appropriate volumes

6.5 Analytical balance

7.0 REAGENTS

7.1 Hexane

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SL SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in SL SOP AN43:*Standard Preparation*.

The lab should purchase certified solutions from SL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SL SOP AN43 for guidance for standard preparation from neat materials.

8.1 The recommended calibration standards are listed in Appendix A, Table 1. Prepare these standards at the stated concentrations in hexane.

8.2 The surrogate compound, 13C12-Decachlorobiphenyl, is prepared at a concentration of 1.0ug/mL and 1.0mL of this solution is spiked into all samples and QC items prior to extraction.

8.3 The matrix spiking solution contains one PCB congener of each chlorination level except for the nonachlorobiphenyls. The solution is prepared at the indicated concentrations in acetone and 1.0mL of this solution is spiked into all lab spikes and matrix spikes.

COMPOUND	CONCENTRATION (ug/mL)
2-Chlorobiphenyl	2.0
2,3-Dichlorobiphenyl	2.0
2,4,5-Trichlorobiphenyl	2.0
2,2',4,6-Tetrachlorobiphenyl	4.0
2,2',3,4,5'-Pentachlorobiphenyl	4.0
2,2',4,4',5,6'-Hexachlorobiphenyl	4.0
2,2',3,4',5,6,6'-Heptachlorobiphenyl	6.0
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	6.0
Decachlorobiphenyl	10

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP Number	Extraction Technique
Aqueous	EX30	Continuous Liquid-liquid Extraction
Aqueous	EX35	Separatory Funnel
Soils/Sediments and Biological	EX40, PS15	Sonication

9.2 The sample concentration procedures are given in SL SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (SL SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products. Acid cleanup (SL SOP EX60) is recommended as a routine cleanup prior to analysis. Sulfur cleanup may be necessary if the sample extract contains high levels of sulfur.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:

HP-5MS 30m x 0.25mm ID, 0.25um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:

Initial column temperature: 45 C for 1 minutes
Column temperature program 1 : 20C per minute to 150C, hold 1 minute
Column temperature program 2 : 10C per minute to 310C, hold until DCB and 13C12-DCB elute

GC injector parameters .

Injector temperature : 250-260°C
Injector : splitless
Inlet purge time : 0.8 minutes
Injector liner : 4mm ID quartz or 4mm glass, deactivated
Sample injection volume : 2uL

Mass Spectrometer and interface parameters

Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: SIM (see Table 3 in Appendix B for ions to monitor)
Mass range for DFTPP analysis: 35-500amu at 1 scan per second or less.

10.2 Tune Criteria

Twenty nanograms of DFTPP are analyzed at the beginning of each 12 hour clock as a check on the "tune" of the mass spectrometer. The DFTPP analysis is performed using scan analysis and the same tune parameters are used for the SIM analysis of the calibration standards and samples.

10.2.1 Prepare a 10ng/uL solution of DFTPP column evaluation standard. The standard must also contain p,p'-DDT (4,4'-DDT).

10.2.2 Analyze a 2uL aliquot of the 10ng/uL DFTPP solution using the same temperature program that is used for SIM analysis of the calibration standards, samples, and QC samples.

10.2.3 Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.3 Window-Defining Solution and SIM Parameters

10.3.1 Analyze 2uL of the window-defining solutions in the scan mode from 45amu to 500amu at > 1 scan per second. Use the same temperature program that will be used for the SIM analysis of PCBs. The window defining solutions may be analyzed separately or may be combined into a single solution.

10.3.2 Determine the retention times of the first and last eluting congeners at each level of chlorination. The quantiation and confirmation masses are listed in Table 3 of Appendix B.

10.3.3 Set the SIM parameters as follows. Refer to Table 3 of Appendix B for the ion sets.

-Begin data acquisition with ion set #1 before the elution of PCB congener #1, Stop the acquisition of ion set #1 and begin acquisition of ion set #2 approximately 10 seconds before the elution of PCB congener #104.
-Stop the acquisition of ion set #2 and begin the acquisition of ion set #3 approximately 10 seconds after the elution of PCB congener #77..
-Stop the acquisition of ion set #3 and begin the acquisition of ion set #4 approximately 10 seconds after the elution of 4,4'-DDT. (the retention time of 4,4'-DDT is determined from the scan analysis of the DFTPP solution that is analyzed at the beginning of each 12-hour clock.).
-Stop the acquisition of ion set #4 and begin the acquisition of ion set #5 approximately 10 seconds before the elution of PCB congener #208.

10.3.4 Verify the SIM "on/off" times by re-analyzing the window-defining mix by SIM prior to the initial calibration.

10.4 Initial Calibration
After the SIM windows are established and verified and the DFTPP criteria has been met, the initial calibration standards are analyzed. Note that a single PCB congener of each chlorination level is used for calibration and quantiation. Decachlorobiphenyl is used to quantify nonachlorobiphenyls.

10.4.1 Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range.

10.4.2 Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts. The routine volume is 2uL.

10.4.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.4.4The relative response factor for each compound is calculated as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion of the calibration congener
Ais = area of the characteristic ion for Chrysene-d10
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

NOTE: Use Chrysene-d10 as the internal standard unless matrix interferences are encountered. If phenthrene-d10 must be used, the calibration must be re-evaluated and verified using the second internal standard

10.4.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3 .... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.4.6Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\sum_{i-1}^{n_l} \frac{(RRF_i - RRF_{avg})^2}{n-1}}$$

10.4.7Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

- If the %RSD of each target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples.

- If the %RSD of the target compound is greater than 20%, the curve should be evaluated for errors and one or more standards re-analyzed. Take corrective action until the %RSD of each target is less than 20%.

10.4.8 Performance Criteria
In addition to meeting the calibration criteria, the following performance criteria must also be met for the mid-level standard.

-Mass abundance ratios of all calibration congeners within acceptance range
(see Table 4,Appendix B)
-Baseline separation of PCB congener #87 from congeners #154 and #77
-Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241
-decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498

10.5 Continuing Calibration Verification
Samples are analyzed only after the DFTPP criteria and the calibration acceptance criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the DFTPP and a mid-level calibration standard prior tot he analysis of samples and after the samples by the analysis and evaluation of a mid-level standard.

10.5.1 The percent difference or percent drift between the continuing calibration RRF and the average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$\%difference = \left|\frac{RRF - RRFavg}{RRFavg}\right| \otimes 100$$

where
RRF = relative response factor from CCV
RRFavg = average relative response factor from initial calibration curve

If the percent difference is less than or equal to 20% for each target compound, the initial calibration is verified.

If the continuing calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the analysis of the continuing calibration standard must be repeated. The analyst must be aware of the 12-hour clock-DFTPP criteria must be met prior to the analysis of the calibration standards. If the continuing calibration standard repeatedly fails the calibration verification criteria, the initial calibration curve must be reanalyzed and reevaluated.

The performance criteria given in Section 10.4.8 must also be met prior to the analysis of samples.

10.6 Sample Analysis
Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.6.1 Add 20uL of the internal standard mix (37.5ug/mL) to each 1-mL aliquot of the sample extract. The concentration of the internal standard in the extract is ng/uL.

10.6.2 Mix the contents of the autosampler vial by inverting several times.

10.6.3 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

10.6.4 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract is diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (2000ug/mL)-Vistd	DF
1000	0	1000	20	1
500	500	1000	10*	2
200	800	1000	16*	5
100	900	1000	18*	10
50	950	1000	19*	20
20	980	1000	20*	50

*assumes dilution of a 1.0mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 0.75ug/mL using 10ul of a 37.5ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 0.75ug/mL. The following equation can be used to determine the volume of the 37.5ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 20uL - \left(\frac{Vext}{Vdil} \otimes 20ul \right)$$

Vistd = volume of 37.5ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

11.1.1 Examine the Selected Ion Current Profiles (SICP) for the internal standards. Confirm that the RT and response of the internal standards are within the acceptance criteria specified in the SOP Summary. If the internal standard retention times have changed significantly or the peaks cannot be located, stop and analysis and correct the problem. Reanalyze any associated samples.

11.1.2 Evaluate the peaks for candidates to be identified as PCBs. A peak is tentatively identified as a PCB if

-The peak falls within the retention time range bordered by the first and last eluting isomer of that chlorination level

-The ratio of the quantitation and confirmation ions are present and the area ratios fall within the acceptance criteria in Appendix B, Table 4. The scans must maximize within one scan of each other. Examine the data for the presence of a coeluting PCB of higher chlorination if both ions and the M-70 ions are present and the ratio does fall within the acceptance limits.

-The areas for the quantiation and confirmation ions must be greater than three times the background noise and must fall within the working range of the calibration curve (must not saturate the detector

-At least one ion in the M-70 cluster must be present

11.1.3 Evaluate each PCB candidate in the Cl-3 to Cl-7 range for the presence of coeluting PCBs containing one or two additional chlorines. An intense M+35 ion at the retention time may indicate a PCB with one additional chlorine and the presence of an intense M+70 would indicate a co-eluting PCB containing two additional chlorines. Use the information in Tables 5 and 6 of Appendix B to correct for the interfering ion(s).

For example, if a Cl-7-PCB and a Cl-5-PCB coelute, the Cl-7-PCB will contribute to the quantiation and confirmation ions for the Cl-5-PCB. Cl-7-PCB produces a cluster of three ions by the loss of two chlorines-ions 322,324, and 326. Two of these ions-324 and 326-are also ions contained in the molecular ion cluster of Cl-5-PCB. To determine the ion 326 and 324 areas produced only by the Cl-5-PCB, calculate the contribution to each and subtract it from the measured areas. See Tables 5 and 6 in Appendix B for the percentage of the interference peak to subtract from the quantiation and confirmation ions. In this example, 164% of the area measured for ion 322 should be subtracted from the area measured for ion 324 and 108% of the area measured for ion 322 should be subtracted from ion 326.

NOTE: A coeluting PCB with one more chlorine will affect only the quantiation ion (Table 6).
The interference from a coeluting PCB containing one more chlorine, due to the natural abundance of 13C12, is small and can usually be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of a another PCB containing one more chlorine.

11.2 Calculations for Samples-Internal Standard Technique

These calculations assume that the same volume is injected for standards and samples.

11.2.1 Aqueous Samples

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where

Ax = sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/mL)
RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
V = volume of sample extracted (L)
DF = dilution factor

The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where

F = final volume of extract (mL)
Fqap = 1.0mL
Vqap = 1.0L
V = volume of sample extracted
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax = sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/mL)
RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100
DF = dilution factor

The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where

F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The SL CQAP assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching*. SL SOP AN02 also describes the procedure for evaluating batch-specific QC. The attached SOP summary and Table 13.1 in the SL Corporate QA Plan provide guidance for evaluating sample data.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each laboratory must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration are the preparation and analysis of spiked reagent water. The criteria for IDOC accuracy and precision are the accuracy and precision criteria listed in Table 5 of the SL QAP.

12.3 Method Detection Limit

The method detection limit is determined by each lab annually in accordance with SL SOP CA90:*Procedure for Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. See Section 10 of the current SL Quality Assurance Plan.

14.0 TROUBLE-SHOOTING-Trouble-shooting items will be added at a later time.

15.0 REFERENCES

15.1 *Savannah Laboratories' Comprehensive Quality Assurance Plan* and Savannah Laboratories' *Corporate Quality Assurance Plan*, current revisions.

15.2 *Method 680: Determination of Pesticides and PCBs in Water and Soils/Sediment by Gas Chromatography/Mass Spectrometry.* November 1985. Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, USEPA, Cincinnati, OH

APPENDIX A

TABLE 1 CALIBRATION STANDARDS

CALIBRATION COMPONENTS	CAL 1	CAL 2	CAL3	CAL4	CAL5
Calibration Congener					
2-chlorobiphenyl (1)	0.10	0.50	1.0	2.0	5.0
2,3-dichlorobiphenyl(5)	0.10	0.50	1.0	2.0	5.0
2,4,5-trichlorobiphenyl(29)	0.10	0.50	1.0	2.0	5.0
2,2',4,6-tetrachlorobiphenyl(50)	0.20	1.0	2.0	4.0	10
2,2',3,4,5'-Pentachlorobiphenyl (87)	0.20	1.0	2.0	4.0	10
2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.20	1.0	2.0	4.0	10
2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.30	1.5	3.0	6.0	15
2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	0.30	1.5	3.0	6.0	15
Decachlorobiphenyl	0.50	2.5	5.0	10	25
Retention Time Congeners					
3,3',4,4-tetrachlorobiphenyl(77)	0.20	1.0	2.0	4.0	10
2,2',4,6,6'-Pentachlorobiphenyl (104)	0.20	1.0	2.0	4.0	10
2,2',3,3',4,5,5',6,7'-nonachlorobiphenyl(208)	0.40	2.0	4.0	8.0	20
Surrogate					
13C12-Decachlorobiphenyl	0.50	2.5	5.0	10	25
Internal Standards					
Phenathrene-d10	0.75	0.75	0.75	0.75	0.75
Chrysene-d12	0.75	0.75	0.75	0.75	0.75

TABLE 2 –First and Last Eluting Isomers

Congener	First Eluting Isomer	Last Eluting Isomer
Cl-1	2-chlorobiphenyl	4-Chlorobiphenyl
Cl-2	2,6-dichlorobiphenyl	4,4'-dichlorobiphenyl
Cl-3	2,2',6-trichlorobiphenyl	3,4,4'-trichlorobiphenyl
Cl-4	2,2',6,6'-tetrachlorobiphenyl	3,3',4,4'-tetrachlorobiphenyl
Cl-5	2,2',4,6,6'-pentachlorobiphenyl	3,3',4,4',5-pentachlorobiphenyl
Cl-6	2,2',4,4',6,6'-hexachlorobiphenyl	3,3',4,4',5,5'-hexachlorobiphenyl
Cl-7	2,2',3,4',5,6,6'-heptachlorobiphenyl	2,3,3',4,4',5,5'-heptachlorobiphenyl
Cl-8	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2,3,3',4,4',5,5',6-octachlorobiphenyl
Cl-9	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

APPENDIX B
SIM IONS

Table 3-Ions for SIM Acquisition

ION Set 1 (a)	ION Set 2 (b)	ION Set 3 (c)	ION Set 4 (d)	ION Set5 (e)
152	186	248	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	391	462
258	323	360	392	464
290	324	362	394	466
292	326	392	396	496
294	328	394	398	498
	358	396	428	499
	360	398	430	500
	362		432	502

(a) Cl-1 to Cl-4 and Phenthrene-d10
(b) Cl-3 to-Cl-6
(c) Cl5 to Cl-7
(d) Cl-6 to Cl-8 and Chrysene-d12
(e) Cl-8 to Cl-10 and 13C12-DCB

TABLE 4-Approximate Retention Times for PCB Isomer Groups and Calibration Congeners

PCB Isomer Group	Approximate RRT Range	Calibration Congener	Approximate Calibration Congener RRT
Cl-1	0.30-0.35	2-chlorobiphenyl (1)	0.30
Cl-2	0.38-0.50	2,3-dichlorobiphenyl(5)	0.43
Cl-3	0.46-0.64	2,4,5-trichlorobiphenyl(29)	0.54
Cl-4	0.55-0.82	2,2',4,6-tetrachlorobiphenyl(50)	0.56
Cl-5	0.64-0.92	2,2',3,4,5'-entachlorobiphenyl (87)	0.80
Cl-6	0.75-1.1	2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.82
Cl-7	0.88-1.2	2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.88
Cl-8	0.99-1.21	2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	1.03
Cl-9	0.16-1.28	Decachlorobiphenyl	1.3
Cl-10	1.3	Decachlorobiphenyl	1.3

RRT = retention time relative to Chrysene-d12

Table 4 Quantitation and Interference Check Ions

PCB Isomer Group	Quant ION	Confirmation ION	Expected Ratio(a)	Acceptable Ratio(a)	M-70 Confirmation ION	Interference Check ION M+70	Interference Check ION M+35
Cl-1	188	190	3.0	2.5-3.5	152	256	222
Cl-2	222	224	1.5	1.3-1.7	152	292	256
Cl-3	256	258	1.0	0.8-1.2	186	326	290
Cl-4	292	290	1.3	1.1-1.5	220	360	326
Cl-5	326	324	1.6	1.4-1.8	354	394	360
Cl-6	360	362	1.2	1.0-1.4	288	430	394
Cl-7	394	396	1.0	0.8-1.2	322	464	430
Cl-8	430	428	1.1	0.9-1.3	356	498	464
Cl-9	464	466	1.3	1.1-1.5	390		498
Cl-10	498	500	1.1	0.9-1.3	424		
Chrysene-d12	240	241	5.1	4.3-5.9			
Phenathrene-d10	188	189	6.6	6.0-7.2			
13C12-DCB (surrogate)	510	512					

(a) ratio of quantitation ion to confirmation ion

TABLE 5-Corrections for Interference of PCB Containing Two Additional Chlorines

PCB Isomer Group	Quant ION	Confirmation ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area	Percent Ion area to be subtracted from CONFIRMATION ION Area
Cl-3	256	258	254	99	33
Cl-4	292	290	288	65	131
Cl-5	326	324	322	108	164
Cl-6	360	362	356	161	71
Cl-7	394	396	390	225	123

TABLE 6-Corrections for Interference of PCB Containing One Additional Chlorine

PCB Isomer Group	Quant ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area
Cl-2	222	221	13.5
Cl-3	256	255	13.5
Cl-4	292	289	17.4
Cl-5	326	323	22.0
Cl-6	360	357	26.5
Cl-7	394	391	30.9
Cl-8	430	425	40.0

APPENDIX C
680 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Biological	Frozen	Glass or aluminum foil	6 months	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
DFTPP 20ng on column Clock starts at injection	DFTPP 20ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification
Samples and the capping standard must be analyzed within 12 hours of the start of the clock	Samples and the capping standard must be analyzed within 12 hours of the start of the clock
Capping standard	Capping standard

DFTPP CRITERIA

m/z	Ion Abundance Criteria
127	40-60% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass443
442	>40% of mass 198
443	17-23% of mass 442

ANALYTICAL BATCH
SEE SL SOP AN02.

CALIBRATION ACCEPTANCE CRITERIA

Initial Calibration	Continuing Calibration
RRFavg <= 20% RSD	Percent difference <= 20% difference from initial calibration

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 20ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
Initial Calibration-minimum of five calibration standards	After Tune Check and when calibration verification standard fails acceptance criteria.	%RSD <= 20%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Performance Criteria	Evaluate mid level calibration standard each clock	-Mass abundance ratios of all calibration congeners within acceptance range (see Appendix B) -Baseline separation of PCB congener #87 from congeners #154 and #77 -Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241 -decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples and at the end of the analytical sequence	%Difference <= 20%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be within 30% of the previous CCV and within 50% of the initial calibration Areas in samples should be evaluated for gross error . Consult superior	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within Section 5 QAP limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SL SOP AN02 and SL QAP Table 13.1
Lab Control Standard (LCS) - QAP subset	See AN02	All spiked targets within the accuracy criteria in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SL SOP AN02 and SL QAP Table 13.1
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See AN02	All targets within the accuracy and precision criteria in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SL SOP AN02 and SL QAP Table 13.1

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Demonstration of Capability (IDOC)	Per analyst	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	See CA90	Evaluate according to SL SOP CA90	Evaluate according to SL SOP CA90

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Approval Signature:	R. Wayne Robbins R. Wayne Robbins
Title: Corporate QA Manager	Date: 5/24/99

HYDROGEN CYANIDE AND HYDROGEN SULFIDE RELEASED FROM WASTES
(Reactive Cyanide and Sulfide)

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the hydrogen cyanide and hydrogen sulfide released from wastes under the specific conditions given in this SOP. This measurement is used to determine whether the waste exhibits hazardous characteristics of cyanide and/or sulfide released above the threshold limit. The threshold limit for cyanide is 250mg HCN/kg waste and the threshold limit for sulfide is 500mg H_2S/kg waste. This method is not applicable to the determination of total cyanide or total sulfide in waste samples.

1.2 The reporting limits (RL) for hydrogen cyanide and hydrogen sulfide released from waste are given in Section 5 of the Savannah Laboratories' quality assurance plans.

2.0 SUMMARY OF METHOD

2.1 A 10g portion of a well mixed waste is transferred to a specially designed vessel. The vessel is purged with nitrogen to eliminate the residual oxygen and 250mL of 0.01N sulfuric acid is added to the sample under a nitrogen atmosphere. As the acid is added, sulfide and/or cyanide present in the sample may be converted to hydrogen sulfide or hydrogen cyanide. The released gases are swept into a scrubber containing sodium hydroxide and trapped as sodium sulfide or sodium cyanide. After the acid has been added, the sample is allowed to react and mix at room temperature for 30 minutes. After the reaction time has elapsed, the scrubber solution is titrated for sulfide using the procedures in SL SOP GE100 or for cyanide using the procedures in SL SOP GE40, GE45 or GE46.

2.2 Reactive sulfide or cyanide is defined as the sulfide or cyanide released from a waste under the conditions described in Chapter 7, Sections 7.3.3.2 and 7.3.4.2, of SW-846. The addition of 250mL of 0.01N sulfuric acid will not generally be sufficient to overcome the buffering capacity of a waste and to produce a quantitative recovery of sulfide or cyanide. The purpose of this test is to determine if a waste releases sulfide or cyanide, not that the waste contains sulfide or cyanide. A sample with a high pH may contain significant concentrations of sulfide or cyanide and yet pass the reactivity threshold.

2.3 The sample preparation is based on SW846 Chapter 7, Sections 7.3.3.2 and 7.3.4.2.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do no understand or that will put you or others in potentially dangerous situations.

3.2 Hydrogen sulfide and hydrogen cyanide gases are extremely poisonous. Exposure to large amounts of these gases can cause nausea, headaches, diarrhea, and even death. Although very high levels rarely occur in environmental samples, the analyst must be careful when handling these potentially hazardous and toxic samples.

3.3 The odor threshold for hydrogen sulfide is between 0.025ug/L and 0.25ug/L. This means you will smell hydrogen sulfide gas (a rotten egg odor) at levels which are not considered toxic. Hydrogen cyanide has an odor like "almonds". Although the reaction apparatus is a closed, properly vented system, it is imperative that all connections in the apparatus are sealed properly to avoid any loss of the gases. If the "rotten egg" smell or the odor of almonds is detected during the reaction, contact your supervisor immediately for corrective action.

3.4 When massing samples and standards for analysis, the analyst must be equipped with lab coat, safety glasses and latex gloves. Handling of reactive samples and standards prior to distillation and analysis must be done under a ventilation hood or in a well ventilated area.

3.5 Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

3.6 Care must be taken when handling the reaction vessel. The flask contains an acidic solution. Acids can cause skin burn, immediate eye damage and destroy unprotected clothing. Pour waste from the distillation flask through lime rocks (to neutralize the acid) before disposal.

3.7 Special care must be taken when handling sulfuric acid (H2SO4). Acids can cause skin burns, immediate eye damage and destroy unprotected clothing. Lab coats, safety glasses and gloves MUST be worn at all times when handling this acid, regardless of the concentration.

3.8 Heat will be evolved as sodium hydroxide (NaOH) dissolves in water. Sodium hydroxide solutions are caustic and will cause skin burns, immediate eye damage, and destroy unprotected clothing. The analyst must be equipped with lab coat or apron, safety glasses and latex gloves.

4.0 INTERFERENCES

Since this method only determines hydrogen sulfide and hydrogen cyanide gas evolved under the method conditions for the sample specific matrix, interferences are minimal. See the analytical procedures for potential interferences.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Waste samples are collected in wide-mouthed glass jars fitted with Teflon-lined caps. The container must be filled completely to avoid any exposure to air. Waste samples are stored at 4 C+/- 2 C, in complete darkness, until time of analysis. Samples should be analyzed as quickly as possible.

6.0 APPARATUS AND MATERIALS

6.1 Reaction vessel(Figure 1) consisting of the following:

500mL three neck round bottom flask with 24/40 standard taper joints

250mL dropping funnel with teflon stopcock

Rubber stopper

Oval stir bars

Purge gas outlet arm

125mL gas-scrubbing bottles

Tubing - Nalgene autoclavable - 5/16" ID

Stir plate

Nitrogen gas supply and flow regulator

6.2 Top loading balance

6.3 Plastic bags or glass vessels for homogenizing the sample

7.0 REAGENTS

All reagents must be tracked in accordance with SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water - lab generated deionized water (DI water)

7.2 Sodium hydroxide (NaOH) - reagent grade.

CAUTION! THIS COMPOUND IS CAUSTIC! THIS COMPOUND WILL CAUSE SKIN BURNS, IMMEDIATE EYE DAMAGE, AND WILL DESTROY UNPROTECTED CLOTHING!

7.3 Sodium hydroxide (NaOH), 0.25N - Place 800mL DI water in a 1-L volumetric flask. Place a stir bar in the volumetric and place on a stir plate. Begin stirring DI water. Slowly add 10g of NaOH. Continue stirring until the solid is completely dissolved, and the solution has cooled to room temperature. Remove the stir bar with a stir bar retriever, and dilute to volume with DI water. Transfer this solution to a plastic or glass container for storage.

7.5 Sulfuric acid (H2SO4), concentrated - reagent grade.

CAUTION! THIS COMPOUND IS ACIDIC! IT WILL CAUSE SKIN BURNS, INSTANT EYE DAMAGE AND DESTROY UNPROTECTED CLOTHING!

7.6 Sulfuric acid (H2SO4), 0.01N - Place approximately 800mL DI water in a 1-L volumetric flask. Carefully add 2.8mL c.H2SO4. Dilute to volume with DI water and mix well. Withdraw 100mL of this solution and dilute to 1.0L with DI water to make the 0.01N H2SO4. Transfer this solution to a plastic or glass container for storage.

8.0 STANDARDS

The preparation of the standards must be in accordance with SL SOP AN41: *Standard Material Traceability*.

8.1 Sulfide Stock Standard (10,000mg/L) - preparation and standardization is given in SL SOP GE100.

8.2 Hydrogen Sulfide Lab Control Standards (LCS):

0.25mL of the 10000mg/L stock solution is added to an empty reactivity vessel and analyzed. The weight of sample is assumed to be 10.00g and the theoretical (true) concentration (Tc) is:

$$Tc(mg/kg) = \frac{V \otimes C}{W} \otimes \frac{1000g}{kg} \otimes \frac{1L}{1000mL} \otimes \frac{1.063mgH2S}{mgS}$$

$$Tc(mgS/kg) = \frac{0.25mL \otimes 10000mgS/L}{10.0g} \otimes \frac{1000g}{kg} \otimes \frac{1L}{1000mL} \otimes \frac{1.063mgH2S}{mgS} = 266mgH2S/kgwaste$$

where

V = volume of spike solution (mL)
C = concentration of the sulfide spiking solution (mg/L)
W = weight of sample (g)

If the concentration of the stock is not 10000mg/L, V is calculated as:

$$V = 0.25mL \otimes \frac{10000mg/L}{Cs}$$

where

Cs = concentration of the stock standard (mg/L)
V = volume added to the reactivity vessel (mL)

NOTE: Titrate the entire scrubber sample for the LCS.

8.3 Cyanide stock solution (1000ppm) - preparation and standardization is given in the referenced analytical SOPs.

8.4 Hydrgen cyanide Lab Control Standard (LCS):

2.5mL of the 1000mg/L stock solution is added to an empty reactivity vessel and analyzed. The weight of sample is assumed to be 10.00g and the theoretical (true) concentration (Tc) is:

$$Tc(mg/kg) = \frac{V \otimes C}{W} \otimes \frac{1000g}{kg} \otimes \frac{1L}{1000mL} \otimes \frac{1.038mgHCN}{mgCN}$$

$$Tc(mgCN/kg) = \frac{2.5mL \otimes 1000mgCN/L}{10.0g} \otimes \frac{1000g}{kg} \otimes \frac{1L}{1000mL} \otimes \frac{1.038mgHCN}{mgCN} = 260mgHCN/kgWaste$$

where

V = volume of stock standard (mL)
C = concentration of stock standard (mg/L)
W = weight of sample (g)

If the concentration of the stock is not 1000mg/L, V is calculated as:

$$V = 2.5mL \otimes \frac{1000mg/L}{Cs}$$

where

Cs = concentration of the stock standard (mg/L)
V = volume added to the reactivity vessel (mL)

9.0 SAMPLE PREPARATION

9.1 Apparatus setup. Prepare distillation setup as shown in Figure 1.

9.1.1 Using clamps, attach the 500mL three neck flask over a stir-plate. Place an oval stir bar in the three neck flask.

9.1.2 With the stopcock closed, carefully fill the dropping funnel with 250mL of 0.010N $H2SO4$. Place the rubber stopper in the top of the dropping funnel. Place the dropping funnel in the center neck of the three neck flask. Use a clamp to provide support for the dropping funnel.

9.1.3 Into each of two gas scrubbing bottles, add 50mL 0.25N NaOH. Add enough water to bring the volume in the gas scrubbing bottles to approximately 3/4 full.

9.1.4 Attach the prepared gas scrubbing bottles, as shown in Figure 1, to the right hand neck of the three neck flask.

9.1.5 Connect the inlet nitrogen tube to the left hand neck of the three neck flask.

9.1.6 Turn nitrogen gas on at the tank. Adjust the regulator so that 3-5 bubbles per second are being produced in each of the gas scrubbers.

9.1.7 If gas scrubbing bottles do not produce bubbles, check the system for leaks at the joints.

9.1.8 While QC and samples are being prepared, purge the system for a minimum of 15 minutes.

9.2 Sample Preparation

For each batch of twenty or fewer samples, a method blank, a lab control standard, and a sample duplicate (if there is sufficient sample for the duplicate) must be prepared and analyzed.

9.2.1 Remove the nitrogen inlet tube. Using a volumetric pipet transfer the 0.25mL of sulfide or 2.5 mL of cyanide stock solutions into the three neck flask through the nitrogen inlet tube. Replace the nitrogen inlet tube.

9.2.2 Label one of the distillation setups which has had sulfide spike added as SLCS. Record the LCS ID, and the LCS mg H2S/kg waste true (theoretical) value in the reactivity distillation log.

9.2.3 Label one of the distillation setups which has had CN spike added as CN LCS. Record the LCS ID and the LCS mg HCN/Kg waste true (theoretical) value in the reactivity distillation log.

9.2.4 Label one of the reaction vessels as the method blank. No sample is added to this vessel. The method blank for sulfide or cyanide reactivity is a measure of the contamination due the reagent and reaction procedure.

9.2.5 Under a ventilation hood, place the entire sample aliquot submitted in either a plastic resealable baggie or into a larger glass container. Homogenize the sample. Break up any clumps of clay, sand, grass, etc. which may cause high variances in the reproducibility of the method. Any large rocks may be discarded.

9.2.6 From the homogenized sample, mass out 10.00g of the waste sample on a top loading balance.

9.2.7 Remove the nitrogen inlet tube and place the sample into the three neck flask. (DI water may be used to facilitate this transfer). Replace the nitrogen inlet tube.

9.2.8 Record the sample ID, sample description, and sample weight (to two decimal points), in the reactivity distillation log.

9.2.9 After the samples, the method blank, and the LCS have been transferred into the reaction vessels, purge each vessel for five minutes with nitrogen prior to the addition of the acid to remove any residual oxygen in the vessel.

9.2.10 Open the stopcock to the dropping funnel, and allow the 0.010N H2SO4 to flow into the three neck flask at a rate of approximately 3 drops per second. Start the stirring as the acid is entering the flask. The solution should not form a vortex when stirring. If a vortex is present immediately slow the stir plate speed.

NOTE: It is critical that the stirring speed remain constant throughout the course of the test, so try to avoid a vortex from forming.

9.2.11 The test time begins when all of the acid has been added to the vessel. Close the dropping funnel stopcock after all of the acid has been added. Record the start time in the reactivity distillation log.

9.2.12 After 30 minutes, discontinue the nitrogen flow, and record the test end time in the reactivity distillation log .

9.2.13 Disconnect the gas scrubbers. Pour both scrubber solutions into a 250mL volumetric flask. Dilute to volume with DI water.

9.2.14 Transfer the scrubber solutions to a plastic 250mL bottle labeled with the sample ID, batch ID, date distilled and analysts initials.

10.0 PROCEDURE

Analyze the scrubber solution for sulfide by SL SOP GE100. Cyanide present in the scrubber solution may be analyzed by SL SOPs GE40, GE45, or GE46.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 The releasable sulfide concentration in the sample is calculated as follows:

$$mgH2S/kg\ waste = \frac{(A \times B)}{W} \times 1.063 \times 1000g/kg$$

where

A = mg S/L determined in scrubber solution
B = final volume of scrubber solution in liters (usually 0.250L)
W = weight of waste tested (grams)
1.063 = 34.080mg H2S/32.064mg S

11.2 The releasable cyanide concentration in the sample is calculated as follows:

$$mgHCN/kg\ waste = \frac{A\ x\ B}{W}\ x\ 1000g/kg\ x\ 1.039$$

where

A = cyanide concentration in the scrubber solution, mg/L
B = final volume of scrubber solution in liters (usually 0.250L)
W = weight of waste tested (g)
1.039 = 27.026 mg HCN/26.018 mg CN

11.3 The percent recovery of the lab control standard is calculated as follows:

$$\%recovery(REC)\ \frac{Clcs}{Tlcs}\ x\ 100$$

where

(Clcs) = concentration of the LCS determined
(Tlcs) = theoretical value of the LCS

11.4 A sample duplicate is performed for every batch of samples if sufficient volume is submitted. The relative percent difference (%RPD), a measure of precision, is calculated for the sample/sample duplicate pair as follows:

$$\%RPD = \left| \frac{(C1 - C2)}{\frac{(C1 + C2)}{2}} \right| \otimes 100$$

where

C1 = concentration of the sample
C2 = concentration of the sample duplicate

12.0 QUALITY ASSURANCE/QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are distilled and analyzed together. The QC items for an analytical batch consist of a method blank, a lab control standard (LCS), and a sample duplicate. If sufficient sample was not submitted to perform a sample duplicate, it must be indicated in the distillation log.

12.2 The method blank is performed with no sample and is used to measure any contamination that is due to the reagents, glassware preparation, or analysis. The method blank should be less than the CQAP reporting limit. If not, any associated sample with positive hits will be reanalyzed.

12.3 The lab control standard is a known concentration of sulfide or cyanide added to an empty reaction vessel and carried through the entire preparation and analytical procedure as a check on the accuracy of the process. The LCS also checks whether leaks are present in the system. If the LCS is not recovered within the CQAP limits, the associated samples must be reanalyzed.

12.4 A sample duplicate is analyzed for each batch as a check on the precision of the entire preparation and analytical process. The result for the duplicates should agree within the limits specified in the CQAP; that is, the %RPD should be less than the CQAP limit. Reanalysis is not required if both duplicates are below the regulatory threshold.

13.0 TROUBLESHOOTING

No items in this section for this revision

14.0 PREVENTIVE MAINTENANCE

No items in this section for this revision.

15.0 REFERENCES

15.1 *Test Methods for Evaluating Solid Waste, Third Edition;* U.S.EPA Office of Solid Waste an Emergency Response: Washington, DC, July 1992.

15.2 *Savannah Laboratories' Comprehensive Quality Assurance Plan,* and *Savannah Laboratories' Corporate Quality Assurance Plan,* current revisions.

SOP SUMMARY FOR REACTIVE CYANIDE AND REACTIVE SULFIDE

This document describes the general procedures and SL policy for the analysis of waste samples for reactive cyanide and reactive sulfide. This procedure will not be used for the analysis of wastes or other matrices that have been chemically preserved prior to analysis. The preservation alters the conditions of the procedure for the releasable parameters. Preserved samples will be analyzed by the procedures for total cyanide and total sulfide.

SUMMARY OF METHOD

Parameter	Hazardous Threshold
Reactive Cyanide	250 mg/kg
Reactive Sulfide	500 mg/kg

Reactive cyanides and reactive sulfides are measurements of the hydrogen cyanide or hydrogen sulfide released from a waste when the waste is subjected to the test conditions specified in Chapter 7 of SW-846. The test is performed in two steps: 1) addition of acid to the waste and collection of any generated cyanide or sulfide gases in a sodium hydroxide scrubber solution; and 2) analysis of the scrubber solution for cyanide and sulfide.

1). Ten grams of waste are placed in a specially designed vessel. Nitrogen is purged through the vessel to remove residual oxygen. 250mL of 0.01N H_2SO_4 are added to the vessel under N_2 and allowed to react for 30 minutes. The generated cyanide and/or sulfide vapor is trapped in scrubber tubes containing 0.125N NaOH.

2) The cyanide trapped in the scrubber solution is analyzed by SW-846 Method 9014 and the sulfide is analyzed by Method 9034. The cyanide in the scrubber solution should have few interferences. The scrubber solution is screened for the presence of sulfide using lead acetate paper prior to analysis.

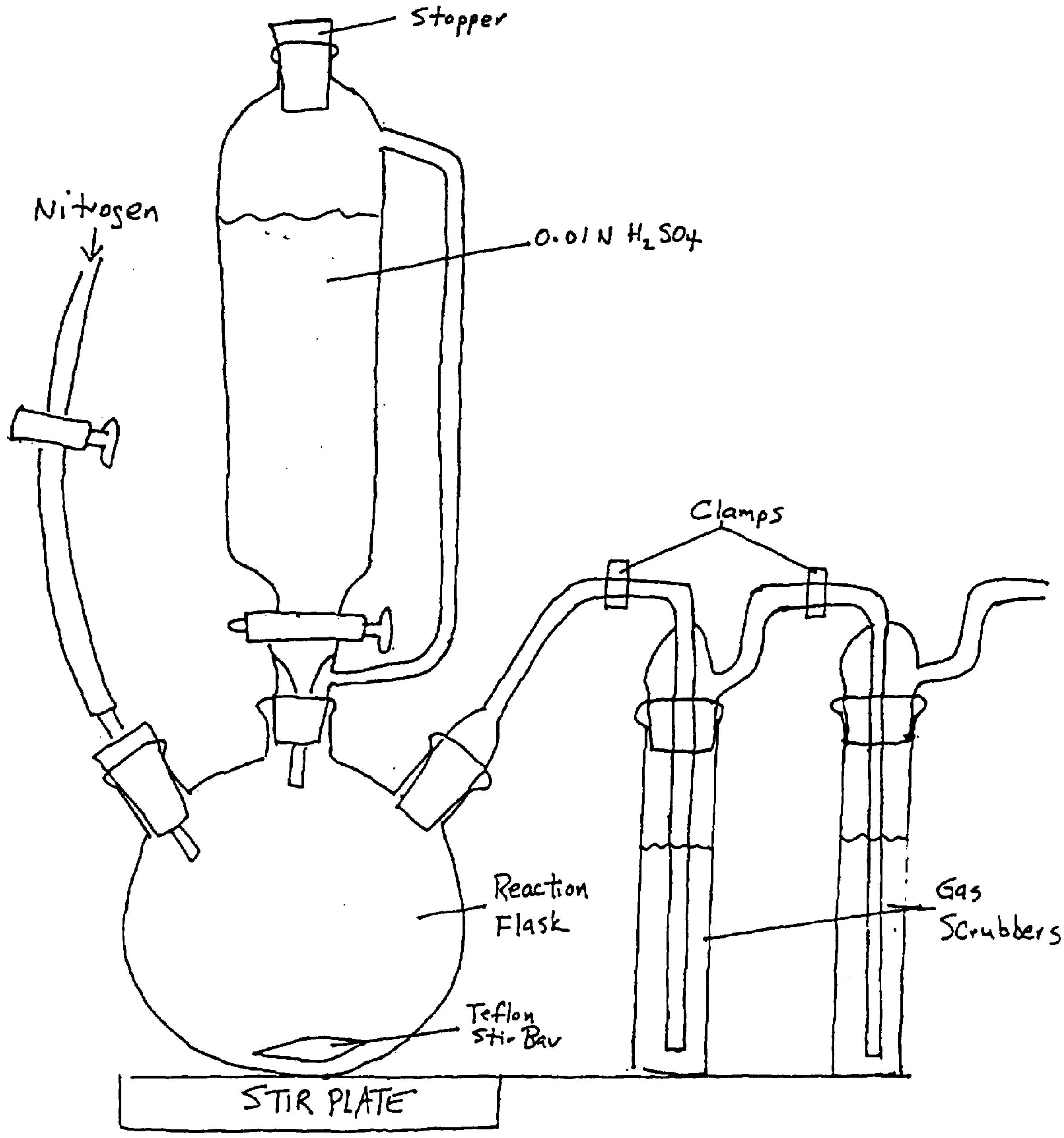
Matrix spikes are not performed or required on the waste since the addition of basic spiking solutions containing cyanide or sulfide would alter the test conditions. The test for the reactive cyanide or reactive sulfide is carried out using an acid concentration that may not be sufficient to neutralize the basic spiking solution and to form the releasable hydrogen cyanide and hydrogen sulfide. In most cases, the addition of the acid to the waste results in only mildly acidic conditions - pH 3 - 4. The QC items for each batch of twenty samples are a method blank, a sample dupicate, and a lab control standard.

QA/QC for Reactive Cyanide and Reactive Sulfide				
Parameter	**QC Check**	**Frequency**	**Acceptance Criteria**	**Corrective Action**
C,S(reactive)	Blank	Per batch	<RL (SL CQAP)	- Reanalyze blank and associated samples if samples also above RL.
C,S(reactive)	Sample duplicate	Per batch	<RPD (SL CQAP)	- Reanalyze if %RPD > 50%
C,S(reactive)	Lab Control Standards	Per batch	Recovery greater than 50%	-Reanalyze -Prepare new standard and reanalyze -Reanalyze associated samples
C,S(reactive)	Initial demonstration of recovery	Per analyst	Recovery greater than 50%	- Reanalyze
C(9014)	Standardization of titration solution	Weekly	Within 20% of target normality	-Remake and/or restandardize the solutions
S(9030)	Standardization of titration solution	Weekly	Within 20% of target normality	-Remake and/or restandardize the solutions

C = Cyanide S = Sulfide

SL SAVANNAH LABORATORIES & ENVIRONMENTAL SERVICES, INC.

Figure 1


Stopper
Nitrogen
0.01 N H_2SO_4
Clamps
Reaction Flask
Gas Scrubbers
Teflon Stir Bar
STIR PLATE

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Approval Signature:	R. Wayne Robbins
Title: Corporate QA Manager	Date: 4/13/99

pH ELECTROMETRIC MEASUREMENT OF WATER, SOILS, AND WASTES

1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to determine the pH of aqueous samples and soil and waste samples. Aqueous samples include monitoring wells, wastewater, and industrial waste such as influents and effluents. Waste samples include solids, sludges, or non-aqueous waste. The possible range pH is 1 to 14.

This SOP also contains procedures for determining pH with pH paper. pH paper can be used to determine if a sample is properly preserved, if a sample has been adjusted to the proper range for extraction, digestion, or leaching, or to approximate the pH before the pH electrode is employed.

1.2 pH is defined by the following equation:

$$pH = -1 (\log [H^+])$$

This shows that pH is a logarithmic function; that is, an increase or decrease of one pH unit represents a ten-fold change in hydrogen ion concentration. The following table demonstrates the relationship between pH and hydrogen ion concentration:

pH	Hydrogen Ion Concentration
1.0	0.10 (1×10^{-1})
2.0	0.010 (1×10^{-2})
3.0	0.0010 (1×10^{-3})
4.0	0.00010 (1×10^{-4})
5.0	0.000010 (1×10^{-5})
6.0	0.0000010 (1×10^{-6})
7.0	0.00000010 (1×10^{-7})
8.0	1×10^{-8}
9.0	1×10^{-9}
10.0	1×10^{-10}
11.0	1×10^{-11}
12.0	1×10^{-12}
13.0	1×10^{-13}
14.0	1×10^{-14}

2.0 SUMMARY OF METHOD

2.1 The pH of an aqueous sample is determined potentiometrically using a combination electrode with temperature compensation. A soil or waste sample is mixed with reagent water. The pH of the solution is measured with the electrode. This procedure may not be used to determine whether a non-aqueous material exhibits the hazardous characteristic of corrosivity (see Chapter 7 of SW-846 Section 7.2).

2.2 The pH meter/electrode is calibrated using a series of certified buffer solutions that bracket the pH of the sample. This procedure for an aqueous sample is based on EPA Method 150.1, SW-846 Method 9040, and SM4500-H+. This procedure for a soil or waste sample is based on SW-846 Method 9045C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or will put you or others in a potentially hazardous situation.

3.2 The analyst should wear a lab coat or apron, gloves, and eye protection when handling the pH buffers and samples.

3.3 MSDS (Material Safety Data Sheets) are available for each reagent and standard used in the lab. The analyst should be familiar with the information supplied in the MSDS.

4.0 INTERFERENCES

4.1 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping with a Kimwipe moistened with hexane followed by rinsing with reagent water. Additional cleaning with hydrochloric acid may be required if the response is sluggish after cleaning with hexane. See Standard Methods 4500-H^+ Section 5b.

4.2 Temperature effects are minimized by the use of a meter/electrode confirmation that automatically compensates for temperature. The temperature of the samples should be at or near the same temperature as the buffer solutions.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous samples for pH measurement should be collected in 100-mL plastic containers. Waste or soil samples for pH measurement are routinely collected in a 100ml glass or plastic container. All containers should be stored at 4°C ± 2°C until analysis. The pH must be determined as soon as possible after collection.

6.0 APPARATUS AND MATERIALS

6.1 pH Meter: Orion Model 501 or equivalent instrument with combination electrode (Orion 91-55 or equivalent) with temperature compensation.

6.2 50ml beakers or other suitable container

6.3 Magnetic stirrer and Teflon-coated stir bars

6.4 Analytical Balance

6.5 pH Paper - wide and narrow range

7.0 REAGENTS

Reagent Water - Lab generated deionized water

8.0 STANDARDS

8.1 Certified pH buffers to bracket pH range of samples. Suggested buffers are 2.0, 4.0, 7.0, 10.0, and 13.0.

8.2 Check Standard: certified solution from ERA or other vendor.

9.0 SAMPLE PREPARATION

9.1 Sample Preparation of Aqueous Samples

There are no preparation steps for the determination of pH in aqueous samples.

9.2 Sample Preparation of Soil Samples

If there is insufficient soil to use 20g, a smaller aliquot can be used if the 1:1 ratio of sample to water is maintained.

9.2.1 To 20g of soil in a 50ml beaker, add 20ml of reagent water. Add a magnetic stir bar to the beaker and place the beaker on the magnetic stir plate. Stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices. If the ratio of water to sample is greater than 1:1, include this information on the reported results.

9.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended material to settle out from the suspension or filter or centrifuge to obtain the aqueous phase for pH measurement.

9.3 Sample Preparation of Waste Materials

9.3.1 To 20g of waste sample in a 50-mL beaker, add 20mL of reagent water, cover, and continuously stir in the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices. If the ratio of water to sample is greater than 1:1, include this information in the reported results.

9.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge to obtain aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the analysis again using 20g of waste and 40mL of reagent water. Include this water to sample ratio with the results.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material. (See Standard Methods 4500-H^+, Section 5b. or SW-846 Method 9045C, Section 3.3).

10.0 PROCEDURE

SEQUENCE
Calibrate with 2 buffers
Check pH with third buffer
Analyze check solution
10 sample determinations
Check Solution
10 sample determinations
Check Solution

10.1 Routine Calibration

This procedure describes the calibration for the range of pH 4 to pH 10 since most pH measurements will fall into that range. Make sure that the pH meter has warmed up and that pH is the selected mode of operation. The lot numbers of the pH buffers must be recorded on the pH data sheet.

10.1.1 Place the pH 7.0 buffer in a beaker on the magnetic stir plate and place the pH electrode in the buffer solution. The electrode should be immersed in the buffer but should not come in contact with the Teflon-coated stir bar.

10.1.2 Allow the solution to stir slowly while the measurement is being made. Adjust the "standardize" or "calibrate" knob on the meter until the pH reads 7.0 ± 0.1.

10.1.3 Rinse the pH electrode with reagent water and place the electrode in the pH 4.0 buffer. Allow the solution to slowly stir while the measurement is being made. Adjust the "slope" or "temperature" knob to bring the meter reading to 4.0.

10.1.4 Rinse the electrode with reagent water and place the electrode in the pH 10.0 buffer. Allow the solution to stir slowly while the measurement is being made. The reading should be 10.0 ± 0.1 pH units. If the buffer does not read within the range, repeat the calibration procedure.

NOTE: It is Savannah Labs policy to consider pH measurements in the 4 to 10 range to be bracketed by two calibration buffers when the meter is calibrated by Section 10.1.

10.2 Non-routine Samples

Samples with pH below 4 and above 10 must be measured with the pH meter/electrode calibrated with buffers that bracket the pH. The pH may be estimated using wide range pH paper and the buffers chosen accordingly. The general procedure is the same described in Section 10.1.

10.3 Sample Analysis

10.3.1 Remove the samples from the refrigerator and allow the samples to come to room temperature. The samples and pH buffers used to calibrate the pH meter/electrode must be at or near the same temperature.

10.3.2 Calibrate and verify the pH meter/electrode. The lot numbers of the pH buffers and check standards must be recorded on the data sheet as described in Section 10.1.

10.3.3 Aqueous Samples

Place an aliquot of the well mixed sample into a beaker on the magnetic stir plate. Make sure that the electrode is immersed in the sample but does not contact the Teflon-coated stir bar.

10.3.3.1 Allow the sample to slowly stir while the pH measurement is being made. Record the pH to the nearest 0.1 pH unit and temperature of the sample after the reading has stabilized.

10.3.4 Soil and Waste Samples

Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

10.3.5 Rinse the electrode with reagent water. Analyze all of the samples in the analytical batch according to the sequence listed earlier in this section. Record the pH ot the nearest 0.1 pH units and record the sample temperature at the time of the analysis.

10.3.6 After all measurements have been made, return the electrode to the 7 buffer or electrode storage solution and set the meter to "standby." The meter should be left "on" when not in use.

10.4 Use of pH Paper

pH paper provides a quick and easy way to approximate the pH of a sample. pH paper can be used to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

10.4.1 pH paper should be checked upon receipt and quarterly to make sure that it is functioning properly.

-Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
-Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper
-Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

10.4.2 Determination of pH with pH Paper

Dip a glass rod or disposable Pasteur pipet into the sample and touch the rod or pipet to the pH paper. Compare the color to the reference.

NOTE: Do not dip the pH paper into a sample. The pH paper dye can bleed into the sample and affect sample results.

11.0 CALCULATIONS

The measurement of pH requires no calculation since the reading is taken from the meter. The calculation of percent recovery of the check standard and precision of pH is more complex than it first appears because the pH scale is a logarithmic function. The pH must be converted back to a concentration prior to the calculation of accuracy and/or precision since slight differences in the pH represent large differences in concentration.

11.1 Calculation of hydrogen ion concentration from a pH measurement.

$$pH = -1(\log[H^+])$$
$$\frac{pH}{-1} = \log[H^+]$$
$$anitlog\,(\frac{pH}{-1}) = [H^+]$$

A calculator that can perform log functions is very handy to make this calculation:

1) enter the pH and change the value to a negative.
2) Take the antilog of the number. (For most calculators that will mean using the 10^x key).

$$\%Rec = \frac{H}{H_T} x\,100$$

11.2 The percent recovery is calculated:
where

H = hydrogen ion from pH measurement
H_T = theoretical hydrogen ion concentration

EXAMPLE
A check standard is analyzed and the pH is determined to be 8.90. The certified concentration is 9.05. The

$$H_{8.90} = antilog(-8.90) = 1.26\ x\ 10^{-9}$$
$$H_{9.05} = antilog(-9.05) = 8.91\ x\ 10^{-10}$$
$$\%Rec = (\frac{1.26\ x\ 10^{-9}}{8.91\ x\ 10^{-10}})\ x\ 100 = 141\%$$

percent recovery is calculated:

This result makes sense because pH 8.90 represents a higher hydrogen concentration than pH 9.05.

11.3 The precision as %RPD is calculated in the routine way as the relative percent difference between two

$$\%RPD = \left|\frac{H_1 - H_2}{(H_1 + H_2)/2}\right| x\,100$$

check standards. When sample duplicates are analyzed, the pH must first be converted to hydrogen ion concentration before the %RPD can be calculated:
where

H_1 = hydrogen ion concentration of replicate 1
H_2 = hydrogen ion concentration of replicate 2

EXAMPLE
Two aliquots of the same sample are analyzed and the pH measurements are 8.90 and 9.00. The %RPD is calculated:

$$H_{8.90} = antilog[-8.90] = 1.26 \times 10^{-9}$$

$$H_{9.00} = antilog[9.00] = 1.0 \times 10^{-9}$$

$$\%RPD = \left|\frac{(1.26 \times 10^{-9}) - (1.00 \times 10^{-9})}{(1.26 \times 10^{-9} + 1.0 \times 10^{-9})/2}\right| \times 100 = \left|\frac{0.26 \times 10^{-9}}{1.13 \times 10^{-9}}\right| \times 100 = 23\%$$

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The pH meter/electrode will be calibrated using two pH buffers that bracket the expected range of pH.

12.2 Duplicate sample measurements will be performed on 10% of the samples.

12.3 A check solution from a separate source will be analyzed after the calibration as an initial calibration verification. A control limit of the theoretical pH ± 0.2 pH units will be used. This is equivalent to the pH recovery range of 63-158% over the pH range of 2 - 13. After every ten samples a check solution buffer will be analyzed as a continuing calibration verification. The pH reading should be ±0.2 pH units of the true value. An RPD control limit of 40% will be used to gauge the acceptability of sample replicates.

13.0 PREVENTIVE MAINTENANCE

No additions to this revision.

14.0 TROUBLESHOOTING

No additions to this revision.

15.0 REFERENCES

1. _Savannah Laboratories' Comprehensive Quality Assurance Plan_ and _Savannah Laboratories' Corporate Quality Assurance Plan_, current revisions.

2. EPA Method 150.1; _Methods for Chemical Analysis of Water and Wastes_, EPA 600/4-79-020.

3. SW-846 Methods 9040 and 9045C; _Test Methods for Evaluating Solid Waste, SW-846 Third Edition_.

4. Standard Method 4500-H^+; _Standard Method for the Examination of Water and Wastewater_, 18th Edition.

Approval
Signature: R. Wayne Robbins
R. Wayne Robbins
Title: Corporate QA Manager
Date: 5/1/98

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TOTAL CYANIDE: AUTODISTILLATION PROCEDURE

1.0 SCOPE AND APPLICATION

This method is used to determine the concentration of cyanide in water, aqueous wastes and leachates. It is used to determine the concentration of both total cyanide and cyanide amenable to chlorination. Cyanide determined by this method has a practical quantitation limit of 0.010 mg/L in liquids and 1.0 mg/kg in soils.

2.0 SUMMARY OF METHOD

In this method, samples are automatically taken up by the autoanalyzer. Metal-cyanide complexes in the samples are dissociated by UV irradiation. The samples are then automatically distilled, buffered, pyridine/barbituric acid is added, and the absorbance of the resulting complex measured at 570 nm.

This method is based on SW-846 Method 9012(1) and EPA Method 335.3 (2), and the soil extraction procedure is based on SW-846 Method 9010A(1).

3.0 INTERFERENCES

Oxidizing interferences may be present in the samples, as indicated by a positive test on KI starch paper. If this type of interference is found, the field crew must reduce these substances by addition of sufficient ascorbic acid to result in a negative KI-starch paper test, plus an additional 0.6 g per liter of sample.

Sulfide is a positive interference in this procedure. Samples are checked for the presence of sulfide upon arrival in the laboratory with lead acetate paper, which indicates sulfide concentrations down to a level of 5-10 mg/L. If sulfide is found to be present by this test, cadmium carbonate, $CdCO_3$, is added to the sample until no more black CdS precipitate forms. Avoid adding an excess $CdCO_3$, as carbonate can hinder the analysis by forming bubbles on the cuvette walls or by causing timing problems with autoanalysis procedures. Filter the samples promptly to limit adsorption or coprecipitation.

Nitrate can be an interference in sufficiently high concentrations (> 10 mg/L) in the presence of certain types of organic matter. Addition of 50 mL of 0.4 N sulfamic acid to the distillation flask will eliminate the effects of this interference.

Thiocyanates may be considered an interference in this procedure, although often they are considered part of the total cyanide concentration.

4.0 APPARATUS AND MATERIALS

Traacs 800 autoanalyzer system, complete with UV lamp, cyanide manifold, and autodistillation system.

5.0 REAGENTS AND STANDARDS

Mixed acid: Carefully add 100 mL of 85% phosphoric acid and 20 mL of hypophosphorous acid to about 800 mL of DI water in a 1-L volumetric flask. Cool, dilute to volume with DI water, and mix thoroughly.

Sodium hydroxide, 0.05 N: Add 2.00 g of solid sodium hydroxide to 800 mL DI water in a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Potassium iodide starch test paper

Sodium hypochlorite: 5.25% (Clorox bleach)

Ascorbic acid (crystals)

Phosphate buffer, pH 5.2: Dissolve 27.2 g of potassium dihydrogen phosphate (KH_2PO_4) and 0.56 g disodium hydrogen phosphate (Na_2HPO_4) in about 800 mL of DI water. Dilute to 1 L with DI water and mix thoroughly. The pH of this solution should be 5.2 ± 0.1.

Chloramine T: Dissolve 0.17 g of Chloramine T in 80 mL DI water in a 100-mL volumetric flask. Dilute to volume with DI water. Prepare fresh daily.

Pyridine/barbituric acid: Weigh out 15.00 g of barbituric acid into a 1-L volumetric flask. Wash the sides of the flask with about 100 mL of DI water. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid, mix, and dilute to volume with DI water. Use a magnetic mixer to dissolve this solution completely. This reagent must be made exactly as stated above. This reagent should be prepared fresh monthly.

Sodium hydroxide solution, 0.25 N: Dissolve 10 g NaOH solid in 800 mL DI water. Cool. Dilute to 1 L with DI water.

Cyanide stock standard, 1000-mg/L: Dissolve 2 g of solid NaOH in about 800 mL DI water in a 1-L volumetric flask. Add 2.503 g of potassium cyanide (KCN), dissolve, and dilute to volume. Standardize by titrating with standard silver nitrate solution. This stock standard should be prepared fresh monthly.

Cyanide intermediate standard, 10-mg/L: Pipet 1 mL of cyanide stock standard into a 100-mL volumetric flask. Dilute to volume with DI water. Prepare fresh daily.

Cyanide working standards: Standards are prepared at concentrations of 10, 40, 70, 100, 300 and 500 μg/L by pipeting appropriate quantities of cyanide intermediate standard and diluting to 10 mL with 0.25 N NaOH solution. Prepare fresh daily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Liquid samples are collected in 120-mL plastic bottles preserved with sodium hydroxide to pH >12 (blue dot) and cooled to 4°C. Soil samples are collected in widemouth jars and cooled to 4°C. Holding time for cyanide samples is 14 days from date of sampling.

Samples are checked for the presence of sulfide with lead acetate paper, as well as proper pH with pH paper, upon their arrival in the lab.

7.0 PROCEDURE

7.1 Amenable Cyanide

Transfer 100 mL or 10 g (or less, depending on cyanide concentration) of sample into 500 mL beaker and place on magnetic stirrer in a fume hood.

Using potassium iodide starch paper, test for residual chlorine (indicated by dark blue color on paper).

If paper is clear, add a dropperful of Clorox to the stirring sample. If the paper turns blue, enough bleach has been added. If the paper does not turn blue, add bleach until it does so.

Set timer for 1 h and check every 15 min with potassium iodide starch paper. Make sure enough Clorox is present to keep paper blue.

After 1 h, add approximately 0.5 g ascorbic acid to stirring liquid. Test with potassium iodide-starch paper until sample tests clear, then add 0.5 g excess ascorbic acid.

Sample is now ready to be analyzed. An untreated (total) sample is also analyzed. If necessary to eliminate interferences, the samples can be manually distilled.

The total cyanide minus the cyanide determined in the chlorinated sample is the amenable cyanide.

7.2 Total Cyanide

Soil and sludge samples are extracted according to method 9010A. A 5-g portion of the soil is weighed out and placed in a 120-mL plastic bottle. A 1-mL aliquot of 50% w/w NaOH solution and 99 mL of DI water is added to the sample. Samples are placed in a rotator and allowed to extract for 16 hours. The extracts are filtered and analyzed as liquid samples.

The instrument is set up as shown in Figure 1. Samples, sample extracts, and QC standards are set up according to the desired protocol. (Refer to Basic Traacs 800 Operating Procedure.) The relative absorbance of a 0.50 mg/L CN standard should be approximately 0.43. Traacs Method 882-90T(3) is followed for the analysis of the samples.

7.3 Calculations

The cyanide concentration of liquid samples is calculated by the autoanalyzer, which has input for dilution factors.

The cyanide concentration of soil samples is calculated by the following equation:

$$CN, mg/kg\ dw = \frac{CN, mg/L \times 0.100\ L}{dry\ wt\ fraction \times g\ sample} \times 1000 \frac{g}{kg}$$

8.0 QUALITY CONTROL/QUALITY ASSURANCE

A calibration curve with a minimum of five points is analyzed daily.

The correlation coefficient of the calibration curve must be ≥ 0.995.

An independent calibration verification standard is analyzed immediately upon calibration (ICV) after every 10 samples (CCV), and at the end of every run.

A blank is analyzed immediately after each calibration verification standard.

A matrix spike and a matrix spike duplicate are analyzed for every batch or every 20 samples, whichever is more frequent.

An extraction blank (sand and extraction fluid) is analyzed for every batch of extracted soil samples, and is considered the method blank for solid samples.

A spiked blank (sand, extraction fluid and spike) is analyzed in duplicate for every batch of extracted soil samples, and is considered the LCS for solid samples.

8.1 Operating Notes

1. Each day prior to initial analysis, flush flow cell with syringe containing DI water.
2. The oil bath unit temperature must be greater than 100° C before starting to pump reagents.
3. Sparging nitrogen flow should be set at approximately 60 (185-195 cc/min).
4. The temperature of the distillation unit should be 150° C ± 2° C during operation.
5. The distillation coil should be removed from the still and cleaned weekly with 10 mL of 0.25 N NaOH, then washed thoroughly with 30-50 mL of DI water.
6. The silicone oil inside the distillation coil should be replaced monthly. Siphon out old oil, wipe, clean and dry chamber completely with paper toweling, and refill with 100 mL of fresh silicone oil. In the event silicone oil is unavailable, mineral oil may be substituted.
7. If leakage occurs around the UV lamp, remove lamp holder and replace all joints within with Acidflex tubing. Seal all joints with epoxy. Make sure epoxy is dry before replacing lamp.
8. Do not allow surfactants to flow through the UV digester or the distillation unit.
9. The pH of waste from the flow cell should be 5.7.

9.0 REFERENCES

1. "Test Methods for Evaluating Solid Waste," Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986.

2. "Methods for Chemical Analysis of Water and Wastes"; U.S. EPA Office of Research and Development: Cincinnati, Ohio, March 1983.

3. "Traacs 800 Method 882-90T": Bran + Luebbe, Technicon Industrial Systems: Tarrytown, NY, March 1990.

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Approval Signature: R. Wayne Robbins R. Wayne Robbins	
Title: Corporate QA Manager	Date: 03/06/98

MIDI DISTILLATION OF WATER AND SOILS FOR THE DETERMINATION OF CYANIDE

1.0 SCOPE AND APPLICATION

This procedure is used to prepare water, soil, and waste samples for the analysis of cyanide. This SOP contains the procedures for the determination of total and amenable cyanide in water and soils. The default procedure for total cyanide in soils is to distill soils in the same manner as liquids. If cyanide amenable to chlorination is requested in soils, the soil is subjected to an extraction procedure prior to the chlorination step and the total cyanide is determined concurrently in the soil leachate.

2.0 SUMMARY OF METHOD

2.1 A measured amount of sample is refluxed with strong acid in a specially designed distillation apparatus-the MIDI distillation apparatus. Cyanide, as hydrocyanic acid (HCN), is released and trapped in an absorber-scrubber containing a sodium hydroxide solution. The cyanide collected in the absorbing solution is determined colorimetrically.

NOTE: The MIDI digestion/distillation unit is used in place of the "macro" units described in the EPA methods. The MIDI digestion/distillation utilizes the same proportion of reagents and sample as in the "macro" units and yields comparable results.

2.2 When cyanide amenable to chlorination is to be determined, the sample is treated with residual chlorine (Clorox) for one hour. After one hour, the excess chlorine is destroyed and the sample is analyzed for cyanide. The cyanide amenable to chlorination is the difference between the total cyanide and the cyanide measured in the sample after treatment with chlorine.

NOTE: If cyanide amenable to chlorination is requested for a soil sample, the sample is extracted with a sodium hydroxide solution. A portion of the leachate is distilled and reported as the "extractable" cyanide and a portion of the leachate is treated with chlorine and distilled. The leaching procedure is required because the direct chlorination of the sample may solubilize metal cyanides that will not be recovered by the direct distillation of the soil.

2.3 This method is based on SW-846 Methods 9010B, and 9013, and EPA Methods 335.2 and 335.4.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Cyanide is extremely poisonous. Although very high levels of cyanide rarely occur in environmental samples, the analyst must be careful when handling these potentially hazardous and toxic samples. Do not add acid to a cyanide sample unless performing one of the preparation steps outlined in this procedure. Acid will cause the evolution of deadly hydrogen cyanide gas.

3.3 The preparation of samples for cyanide amenable to chlorination must be done under a well ventilated hood.

3.4 The standards and reagents used in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment must be used when preparing and using the standards and reagents.

3.5 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. The MSDS contain guidance on the type of hazard that each reagent poses and the safe handling instructions for these materials.

3.6 Care must be taken when handling the distillation apparatus. Before handling glassware that has been in use, check the temperature to make sure that it is not hot. The distillation flask contains an acidic solution. Acids can cause skin burns and destroy unprotected clothing.

4.0 INTERFERENCES

4.1 Chlorine and sulfide may be present in samples. Chlorine will cause a negative interference. Sulfide will cause a positive interference with the colorimetric determination of cyanide. The samples must be screened for chlorine and sulfide upon arrival in the lab.

4.2 Nitrates can cause a positive interference when the nitrate concentration exceeds 10 mg/L and certain organic materials are present in the sample. The addition of 5mL of 0.4 N sulfamic acid to the sample at the time of distillation will eliminate the formation of cyanide from nitrates and organic materials. If nitrates are suspected to be present , samples should be screened for the presence of nitrates upon arrival in the lab.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Soil samples are collected in wide-mouth glass jars equipped with Teflon-lined caps. Soil samples are stored at 4° C (less than 6° C with no frozen samples) until time of analysis. The recommended holding time is 14 days from sample collection.

5.2 Liquid samples are collected in 250mL plastic containers and are preserved by the addition of NaOH to a pH > 12. Liquid samples are stored at 4° C (less than 6° C with no frozen samples) until time of analysis. The holding time is 14 days from the date of collection.

5.2.1 Upon arrival in the laboratory, the pH must be determined to ensure that the sample has been properly preserved. Pour a small volume of the well mixed sample into a small plastic cup and test the pH of the aliquot with narrow range pH paper. If the paper is > 12, the sample is properly preserved. If the pH is < 12, adjust the pH of the sample to > 12 by adding small aliquots of 50% NaOH to the sample container. Shake the sample container to mix the 50% NaOH with the sample. Check the pH of the sample again. Continue adding small aliquots of 50% NaOH to the sample until the pH is > 12.

NOTE: Do not add more preservative than 1% of the volume of the sample. For example, if the sample volume is 500mL, do not add more than 5mL of preservative.

5.2.2 Upon arrival in the laboratory, the sample should be checked for the presence of sulfides. Pour a small aliquot of the sample into a plastic cup. Test the aliquot with lead acetate paper. If the lead acetate paper turns black, add cadmium carbonate to the sample and shake the container to mix. Check the sulfide content again with the lead acetate paper. Continue adding cadmium carbonate to the sample until the lead acetate paper no longer turns black when exposed to the sample.

5.2.3 Upon arrival in the laboratory, the sample must be checked for the presence of residual chlorine. Pour a small aliquot of the sample into a plastic cup. Test the aliquot with potassium iodide starch paper. If the paper turns blue or black, add sodium arsenite to the sample and shake the container to mix. Check the residual chlorine content again with the potassium iodide starch paper. Continue adding sodium arsenite to the sample until the indicator paper no longer turns blue or black when exposed to the sample.

5.2.4 If nitrates are suspected, prior to analysis (but not necessarily upon receipt), samples should be screened for nitrates. Pour a small aliquot of the sample into a plastic cup. Test the aliquot with a Nitrate/Nitrite test strip. If the strip indicates the presence of Nitrate/Nitrite, add 5ml of sulfamic acid solution (described in section 7.7) to 50ml of sample. Note the addition is performed at the beginning of the distillation process.

6.0 APPARATUS AND MATERIALS

6.1 MIDI cyanide distillation apparatus, Model MCV103 or equivalent, with appropriate glassware

6.2 Vacuum Pump

6.3 Tygon tubing

6.4 Volumetric flasks

6.5 Volumetric pipettes

7.0 REAGENTS

The preparation of reagents are tracked according to SL SOP AN44. Do not store reagents in volumetric glassware.

7.1 Reagent water, lab-generated deionized water – See SL SOP AN35 for maintenance procedures for DI water system.

7.2 Clorox bleach (5.25% sodium hypochlorite)

7.3 Potassium iodide (KI)/ starch paper-used to indicate the presence of chlorine

7.4 Sodium arsenite ($NaAsO_2$): reagent grade, used to eliminate interferences from chlorine and to destroy the excess chlorine in the cyanide amenable to chlorination procedure.

7.5 Lead acetate paper-used to indicate the presence of sulfide

7.6 Cadmium carbonate ($CdCO_3$): reagent grade, used to eliminate interferences from sulfides.

7.7 Sulfamic acid (H_2NSO_3H): reagent grade, used to eliminate interferences from nitrates.

7.8 Sulfamic acid solution (0.4 N): Dissolve 40 g of sulfamic acid in a small volume of reagent water in a 1L volumetric flask. Dilute to volume with reagent water. Transfer the reagent to an appropriate container; e.g., a 1L bottle.

7.9 Sodium hydroxide (NaOH): reagent grade

CAUTION: Heat will be evolved as the sodium hydroxide is dissolved in the water. Sodium hydroxide solutions are caustic and will cause skin burns and destroy unprotected clothing.

7.10 Dilution solution (0.25 N sodium hydroxide): Dissolve 10 g of sodium hydroxide in 800 mL of reagent water in a 1L volumetric flask. Dilute to volume with reagent water. Transfer the reagent to a 1L **PLASTIC** container.

7.11 Sodium hydroxide solution (1.25 N): Dissolve 50 g of sodium hydroxide in reagent water in a 1L volumetric flask. Cool and dilute to volume with reagent water. Transfer the reagent to a 1L **PLASTIC** container. Do not store reagents in volumetric glassware.

7.12 Sodium hydroxide (50%): Measure 100 mL of reagent water into a 400mL beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Weigh out 100 g of sodium hydroxide into a plastic container. Add a small quantity of the sodium hydroxide from the container to the reagent water in the beaker on the magnetic stir plate. As the sodium hydroxide dissolves, add more of the sodium hydroxide from the beaker until all 100g has been added. Cool and transfer the reagent to a **PLASTIC** container.

7.13 Sulfuric acid (H_2SO_4): reagent grade, concentrated.

7.14 Sulfuric acid solution (1:1): Measure 500 mL of reagent water into a 2L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly add 500 mL of concentrated sulfuric acid to the reagent water in the beaker on the magnetic stir plate. Transfer the reagent to a 1L bottle. Do not store reagents in volumetric glassware.

CAUTION: Use extreme caution when preparing this solution. Heat will be evolved as the acid and water combine. This solution will cause skin burns and destroy unprotected clothing.

7.16 Magnesium chloride hexa-hydrate ($MgCl_2 \cdot 6H_2O$): reagent grade

7.17 Magnesium chloride solution: While stirring, add 510 g $MgCl_2 \cdot 6H_2O$ in 500 mL of reagent water in a 1L volumetric flask. After the salt dissolves, dilute to volume with reagent water. Transfer the reagent to a 1L bottle. Do not store reagents in volumetric glassware.

8.0 STANDARDS

Sock standards prepared from neat materials. Certificates of analysis or a statement of purity must be received with all neat compounds. All preparation steps must be in accordance with SL SOP AN41:*Standard Material Traceability*. Do not store standard solutions in volumetric glassware.

Potassium cyanide is used to prepare the calibration standards and the spiking solutions. The preparation and standardization of the cyanide solution is given in SL SOP GE40: *Total and Amenable Cyanide: Autoanalyzer Procedure.*

8.1 Cyanide stock standard – approximately 1000 mg/L , prepared from potassium cyanide. See SL SOP GE40 for the preparation and standardization of this stock solution. The KCN cyanide stock is used to prepare the undistilled calibration standards, the distilled calibration standards (also used as LCS), and the matrix spiking solution.

8.2 Preparation of the KCN Cyanide Intermediate Standards

The KCN intermediate is used to prepare the calibration standards (distilled and undistilled), and the spiking solutions. Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking solutions. The following equation can be used:

$$Cs \otimes Vs = Ci \otimes Vi$$

$$Vs = \frac{Ci \otimes Vi}{Cs}$$

where
Vs = volume of stock standard needed to prepare the spiking solution(mL)
Cs = concentration of stock solution(mg/L)
Ci = concentration of intermediate solution to prepare(mg/L)
Vi = volume of spiking solution to prepare(mL)

Preparation of the KCN Intermediate (10mg/L)

Transfer Vs (see above) mL of the KCN cyanide stock standard (approximately 1000mg/L) to a 100mL volumetric flask and dilute to volume with 0.25N NaOH. Two standards are prepared from the KCN and distilled to verify the efficiency of the distillation process. The distilled standards are also evaluated and reported as LCS.

9.0 SAMPLE PREPARATION

9.1 Chlorination Step for Cyanide Amenable to Chlorination

The steps for the chlorination of the samples must be performed under a properly functioning fume hood.

9.1.1 Transfer 100mL of a liquid sample or 100mL of a soil leachate (Section 9.2) to a 500-mL beaker. A smaller volume of sample or leachate can be used if the cyanide concentration is known to be high.

9.1.2 Place the beaker onto a magnetic stir plate in a fume hood. Add a Teflon stir bar to the beaker and stir the sample.

9.1.3 Check the pH of sample with pH paper. The pH of the sample must be maintained at >11 for the duration of the chlorination procedure.

9.1.4 Test the chlorine level in the sample using potassium iodide-starch paper. If the paper turns blue, residual chlorine is present in the sample. If the test paper is clear, add 0.5 mL of Clorox to the stirring sample. Test the sample again with the potassium iodide-starch paper. If the test paper turns blue, enough Clorox has been added. If the paper remains clear, add Clorox until the paper turns blue. An excess of chlorine must be maintained throughout this procedure.

9.1.5 Check the sample every 15 minutes with potassium iodide-starch paper and wide range pH paper.

If the KI paper is blue, check the sample again in 15 minutes. If the paper is clear, add a 0.5mL of Clorox to the sample and check the sample again with the test paper. Continue adding small volumes of Clorox until the test paper remains blue.

If the pH >11, check the sample again in 15 minutes. If the pH <11, add a few drops of 50% NaOH and check the pH again. Continue adding small aliquots of 50% NaOH until the pH remains >11.

9.1.6 Continue stirring the sample for a total of 1 hour, checking the chlorine level and pH every 15 minutes and adjusting as needed.

9.1.7 After 1 hour, add approximately 0.5g of sodium arsenite to the stirring sample. Test the sample with potassium iodide-starch paper. If the test paper remains white, add a second 0.5g portion of sodium arsenite to the sample. If the test paper turns blue, add sodium arsenite in 0.5g increments until the test paper remains white. Add approximately 0.5 g excess of sodium arsenite to the sample.

9.1.8 The sample is now ready to be distilled and analyzed.

9.2 Soil Leaching Procedure

The leaching procedure is the default preparation step for the determination of amenable cyanide in soils. Use the direct digestion/distillation of soils (9.3) for total cyanide.

The pH of the sample must be maintained at pH > 10 throughout the leaching procedure. In most cases, the addition of 200mL of 0.25N NaOH will be sufficient to maintain the pH.

9.2.1 Transfer 10g (+/- 0.5g) of a homogenized soil sample to a labeled, 250mL plastic container. Record the weight of the sample to the nearest 0.1g in the cyanide soil extraction log.

9.2.2 Add 200mL of 0.25N sodium hydroxide to the container. Cap the container and mix thoroughly. Check the pH with narrow range pH paper. If the pH is not greater than 10, add small aliquots of 50% NaOH to bring the pH above 10.

9.2.3 Securely cap the container and place the container in a rotary spinning device for 16 hours.

9.2.4 Remove the containers from the rotator and allow the samples to settle. Allow the sample leachate to settle and decant into a separate labeled container. Check the pH of the leachate. If the pH is greater than 10, the sample is ready for distillation. If the pH is less than 10, the leaching procedure is repeated with a smaller aliquot of solid.

NOTE: If the leachate pH is less than 10, the pH of the sample should be determined. If the sample pH is highly acidic, the sample is not likely to contain cyanide amenable to the leaching procedure.

9.3 Sample Distillation

The distillation batch for cyanide may include both soils and liquids. The same method blank and LCS (distilled standards) can be used for both matrices. MS/MSD are required at a frequency of 5% for all matrices.

9.3.1 Remove the samples from the storage refrigerator and allow the samples to come to room temperature. Complete as much of the distillation log as possible for each batch of samples that are being prepared.

9.3.2 Assemble the distillation apparatus as shown in the manufacturer's manual. Place 50 mL of 0.25 N NaOH into each absorber tube.

9.3.3 Add the samples to the distillation tubes.

9.3.2.1 Mix the liquid sample by inverting the container several times and transfer 50mL of a liquid sample, the cyanide-amenable-to-chlorination sample, or soil leachate to the distillation tube. Record the volume of sample distilled on the cyanide distillation log.

Add a 50mL aliquot of 0.25N NaOH into a distillation unit for the method blank.

Transfer two 50mL aliquots of a sample from the batch into each of two distillation units for the MS and MSD.

Note: If cyanide-amenable-to-chlorination is requested on a soil matrix, the total cyanide is determined on the soil leachate.

9.3.2.2 Homogenize soil samples by stirring with a stainless steel spatula. Add 1g of the well mixed soil sample to the distillation tube. Add 50mL of reagent water to the distillation tube. Record the weight of the sample to the nearest 0.1g on the cyanide distillation log.

-Transfer two 1g aliquots of a sample from the batch into each of two distillation units for the MS and MSD.

-The method blank is performed using only the reagents used for the distillation; that is, add 50mL of 0.25N NaOH to the empty distillation unit and assume a sample weight of 1.0g.

9.3.3 Add 0.5mL of the KCN cyanide intermediate solution (10mg/L) to each matrix spike (MS) and matrix spike duplicate(MSD) sample.

The concentration of cyanide added to the liquid sample is

$$\frac{0.5\,mL \otimes 10\,mg/L}{50\,mL} = \frac{0.0005\,L \otimes 50\,mg/L}{0.050\,L} = 0.10\,mg/L = 100ug\,/\,L$$

The concentration of cyanide added to the soil/solid sample is

$$\frac{0.5\,mL \otimes 10\,mg/L}{(1\,g)(solids)} = \frac{0.00005\,L \otimes 10\,mg/L}{(0.0010\,kg)(solids)} = 5.0\,mg/kg\ (if\ \%\ solids = 100)$$

where (solids) is the decimal equivalent of the percent solids

9.3.3.4 Every day samples are distilled, two calibration standards are prepared, distilled, and analyzed. The volumes of the KCN cyanide intermediate added to prepare the standards are:

$$\frac{0.35\,mL \otimes 10\,mg/L}{50\,mL} = \frac{0.00035\,L \otimes 10\,mg/L}{0.050\,L} = 0.070\,mg/L = 70ug\,/\,L$$

$$\frac{1.0\,mL \otimes 10\,mg/L}{50\,mL} = \frac{0.0010\,L \otimes 10\,mg/L}{0.050\,L} = 0.200\,mg/L = 200ug\,/\,L$$

9.3.4 Connect the glassware and the tubing. Turn on the pump and the condenser water. Inspect each unit to ensure that there are no leaks in the glassware or in the tubing.

9.3.5 Set the timer to 120 minutes and the heating block temperature to 125C.

9.3.6 Add 2mL of the magnesium chloride solution followed by 5mL of 1:1 sulfuric acid to each flask through the distillation head. Rinse the inlet tube with a small aliquot of reagent water.

9.3.7 If the sample contains nitrate, add 5mL of sulfamic acid solution.

9.3.8 After the samples have been distilled, turn off the pump and allow tubes to cool for approximately 20 minutes.

9.3.9 Pour the scrubber solution into a labeled 100mL storage container.

9.3.10 Store the distillate in the dark in the refrigerator until ready to perform the colorimetric analysis. The distillate must be analyzed before the 14-day holding time is up.

NOTE: The hold time is measured from day of collection and **not** from the day of distillation.

10.0 PROCEDURE

The analytical procedure for the determination of cyanide is given in SL SOP GE40.

11.0 CALCULATIONS

The calculations for the determination of cyanide are given in SL SOP GE40.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

SL SOP AN02: *Analytical Batching*, Table 13.1 of the SL QAP, and the SOP Summary provide guidance on evaluating QC and sample data

13.0 PREVENTATIVE MAINTENANCE

13.1 Check the pump to insure that there is sufficient oil for proper operation. Change the oil at a frequency specified by the manufacturer.

13.2 Inspect the glassware and tubing each before and after use for signs of wear and breakage. Pay particular attention to the ground glass joints.

13.3 Change the tubing and connectors if sample or reagents get into lines.

13.4 Check the temperature of the heater block annually.

13.5 Rinse the glassware thoroughly with reagent water to remove all traces of soap. Soap residue that remains in the glassware may cause foaming in the distillation apparatus. The glassware should be rinsed with 10% nitric acid after rinsing with water to remove traces of cyanide and basic active sites and rinsed with deionized water to remove the acid residue.

14.0 TROUBLE-SHOOTING

See manufacturers manual for guidance on repairing the instrument.

15.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste, Third Edition*, SW-846; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

2. *Methods for Chemical Analysis of Water and Wastes*; U.S.EPA Office of Research and Development: Cincinnati, OH, March, 1983.

CYANIDE METHOD SUMMARY

HOLD/STORAGE

Routine Container	Aqueous: 250mL Plastic Soils/Solids: 250-mL Plastic
Preservative	Aqueous: NaOH to pH>12 Soils/Solids: None
Storage	4C (less than 6C with no frozen samples) from collection to analysis
Hold Time	14 days from collection
Interference Checks	Aqueous: Residual chlorine, sulfide, nitrate/nitrite, preservation (pH)

SAMPLE PREPARATION

Aqueous: MIDI, Macro, or custom distillation apparatus with molar volumes consistent with sample size.
Soils/Solids: Direct distillation
Soils/Wastes: Basic leaching procedure followed by distillation in MIDI or Macro distillation apparatus

Matrix	Distillation	Maximum Sample Volume/Weight	Final volume of Distillate
Aqueous or Leachate	MIDI, Macro, or Custom	MIDI - 50mL Macro – 500mL	50ml 250ml
Soils/Solids	Macro, MIDI, or Custom	MIDI-1g Macro - 10g	50mL 250ml

ANALYTICAL SEQUENCE- (9010B/9012A,335.2,335.4)

Initial Calibration- 6 point
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
LCS, method blank, and 7 Sample Measurements
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 Sample Measurements
CCV
CCB
10 Sample Measurements
CCV
CCB

The sequence continues until all of the samples are analyzed or the calibration verification or calibration blank fail the acceptance criteria. The sequence must always end with CCV/CCB.

DISTILLATION BATCH- (9010B/9012A,335.2,335.4)

QC ITEM	Frequency
Method blank	Per batch
Distilled cal standards (also serve as the LCS)	2 per batch-70ug/L and 200ug/L
MS	5% of samples per matrix
MSD	5% of samples per matrix
Samples	Up to twenty samples

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL (6 point curve is routinely analyzed)	Before sample analysis and when continuing calibration verification fail. (see sequence)	Regression curve with correlation coefficient >=0.995; initial calibration verification within +/-10% of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)	After initial calibration and after every 10 sample measurements. (see sequence)	+/-10% of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL SL CQAP Table 5	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank	Per batch	< RL SL CQAP Table 5	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
Distilled standards-(LCS/LCSD)	Per batch	+/-10% of expected value	-Check calculations -Reanalyze distillate -AN02 Decision Matrix
MS/MSD	At a frequency of 5% of samples of the same matrix (one MS and one MSD per twenty samples)	SL CQAP Table 5	-Check calculations -Reanalyze distillate -AN02 Decision Matrix
Initial Demonstration of Capability	Per analyst	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze samples
MDL Study	-SL SOP CA90	-SL SOP CA90	-repeat MDL study

SL SAVANNAH LABORATORIES & ENVIRONMENTAL SERVICES, INC.

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 5/1/98

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IGNITABILITY

1.0 SCOPE AND APPLICATION

This method uses the Pensky-Martens closed-cup tester to determine the flashpoint of field oils and liquids. Liquids containing non-filterable, suspended solids are also tested using this method.

2.0 SUMMARY OF METHOD

The sample is heated at a slow and steady rate while cautiously stirring. A small flame is directed into the cup for every 2□ F increase (the stirrer is turned off each time the flame is directed into the sample). The recorded flashpoint is the lowest temperature at which the test flame ignites the vapor of the sample.

3.0 INTERFERENCES

Sample homogeneity, drafts, or ambient pressure can affect the flashpoint of a sample.

4.0 APPARATUS AND MATERIALS

Pensky-Martens closed flash tester
Fahrenheit thermometer
Closed tester thermometer
Pensky-Martens high range thermometer

5.0 REAGENTS

Calcium chloride, reagent grade
p-Xylene reference standard

6.0 PROCEDURE

Start by cleaning and drying all parts of the cup and all accessories before putting the sample in the cup. All soaps and solvents used in cleaning must be thoroughly rinsed off.

Fill the cup to the fill line with the sample. Put the lid on the cup and place it in the stove. Make sure it is locked tightly, then insert the thermometer. Light the flame and adjust it to a diameter of 4 mm. Supply the heat so that temperature will change at a rate of 2□ F per minute. Turn the stirrer to 90-120 rpm.

Start the ignitability checks 30□ F under the expected flash point. Apply the test flame by operating the mechanism on the cover. This controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 s. Leave it there for 1 s and then raise it out of the cup to the normal position. Do not stir the sample while applying the test flame.

When the test flame application causes a distinct flash inside the cup, read the temperature from the thermometer. This is the flashpoint. Don't confuse a bluish halo or ring that sometimes surrounds the flame with the flash. When a large flame propagates over the surface of the sample inside the cup, the flashpoint has been reached.

Determination of the flashpoint of suspicious solids and highly viscous material is done by bringing the material to be tested and the apparatus to a temperature within 10□ F of 60□ F or 20□ F lower than the estimated flashpoint, whichever is lower. Turn the stirrer to 240 - 260 rpm. Raise the temperature at a rate not less than 2□ F and not more than 3□ F per min. Proceed as directed above.

7.0 CALCULATIONS

Record the ambient barometric pressure at the time of the test. If the pressure differs from 760 mm Hg (101 kPa), correct the flashpoint as follows:

Corrected flashpoint = F + 0.06 (760 - P)
Corrected flashpoint = C + 0.033 (760 - P)

Where

F = observed flashpoint in degrees Fahrenheit
C = observed flashpoint in degrees Celsius
P = ambient barometric pressure, mm Hg

Report the correct flashpoint to the nearest degree.

8.0 QUALITY CONTROL

Duplicates and standard reference materials should be routinely analyzed.

The p-xylene reference standard must be done in duplicate for every sample batch. The average of the two analyses should be within 1.5□ F of the true value.

SOP Document No: GE115: 02.26.99:4
SOP Description: Ion Chromatography

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Title: Corporate QA Manager	Date: April 28, 1999

The following revisions or additions have been made to the referenced SOP.

All changes/additions in **BOLD**
-ICB and CCB must be less than MDL in QAP; the previous revision has the criteria as less than the rerpoting limit (RL)
-a row for method blanks has been added to the summary table -SL SOP CA90 referenced in MDL row.

QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 3 point curve with, lowest point at RL	**Prior to sample analysis and when CCV fails; at least every 6 months**	**Correlation Coefficient of a linear regression curve of 0.99 or greater (SL Policy); Analysis of QCS to +/- 10% of true value**	**-Evaluate ion chromatogram and integrations. Heck calculations -Reanalyze standard(s) -Remake standard(s) and reanalyze**
Initial Calibration Verification (ICV) -mid-range cal std or QCS	**After analysis of initial calibration standards**	+/-10% of true value	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze standards -Remake and reanalyze standard -Recalibrate
Initial Calibration Blank (ICB)	After analysis of CCV	Less than **MDL** in Table 5 of SL CQAP	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze -Remake and reanalyze -Recalibrate
Continuing Calibration Verification (CCV) -mid-range cal std or QCS	After every ten sample and at the end of the sequence	+/-10% of true value	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze standard -Remake and reanalyze standard -Reanalyze associated samples -Recalibrate and reanalyze associated samples

QC Check	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Blank (CCB)	After every ten samples and at the end of sequence	Less than **MDL** in Table 5 of SL CQAP	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze -Remake and reanalyze -Reanalyze associated samples -Recalibrate and reanalyze associated samples
Method Blank (ICB and CCB reported as method blank for liquids where no preparation steps are necessary)	**Per batch of soils or other extractables**	**Less than MDL in Table 5 of SL CQAP**	**-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze -Remake and reanalyze -Reanalyze associated samples -Recalibrate and reanalyze associated samples**
Lab Control Sample (QCS – second source LFB)	Per batch; Analyze in duplicate quarterly	+/-10% of true value (90 - 110% recovery).	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze -Remake and reanalyze -Reanalyze associated samples -Recalibrate and reanalyze associated samples
MS/MSD	Per batch (10% of samples)	+/-20% of spike volume (80 - 120% recovery)	-Evaluate ion chromatogram and integrations. Check calculations -If lab control and blank OK, matrix interference can be assumed -Reanalyze -Remake and reanalyze
Initial Demonstration of Performance	Per analyst	-Prepare cal standards and demonstrate linearity -Analyze QCS (90 – 100%) -perform annual MDL study	-Evaluate ion chromatogram and integrations. Check calculations -Reanalyze for analytes that do not meet criteria.
Method Detection Limit (MDL)	Annually	**See SL SOP CA90**	**SL SOP CA90**
Performance Evaluation (PE) Sample -WS/WP	Quarterly	Within acceptance limits	-Evaluate data and initiate non-conformance reports
Retention Time Window	Each analysis	Define a reasonable window for each analyte or retention time range and apply to each analysis	-Evaluate instrument performance, column, and integration system.
Dilution/Fortification	When high concentration of adjacent peak makes identification difficult	Peak in dilution and/or fortified sample within established window.	-Dilute or fortify (spike) sample at higher dilution factor or concentration.

Approval Signature:	R. Wayne Robbins (signature) R. Wayne Robbins
Title: Corporate QA Manager	Date: 5/1/98

ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

Ion chromatography is a method for the separation of dissolved ionic species using liquid chromatography techniques, along with eluent suppression and conductivity detection. Ion chromatography is applicable to drinking and surface waters, and domestic and industrial waste. The method is most useful for the determination of dirty or highly colored samples that might be problematic for colorimetric determination, or for some instances where a lower limit of detection is required for certain analytes. It is also useful for determining total sulfur, total halogens, and percent sulfur for heat of combustion determinations. This particular method is optimized for the determination of the anions fluoride, chloride, bromide, iodide, nitrate, nitrite, phosphate, sulfate, sulfite, acetate, formate, oxalate, thiosulfate, and bromate.

2.0 SUMMARY OF METHOD

A carbonate/bicarbonate eluent conducts the sample through the chromatography system which consists of a guard column, a separator column, a suppressor column, and a conductivity detector. The guard column screens out potential interferences, the separator column separates the anions, the suppressor column converts carbonate and bicarbonate ions in the eluent to carbonic acid (lowering the conductivity), and the conductivity detector detects the anions from their electrical conductivity in solution. This method is based on EPA Method 300.0(1) SW-846 Method 9056(2).

3.0 INTERFERENCES

Anions whose retention times are similar or substances whose peaks overlap the anion peak of interest interfere with quantitation. Sample dilution and/or eluent change can often resolve these types of problems.

Water, which elutes before the fluoride peak, gives a negative peak and can interfere. This problem can be eliminated by the addition of 1 mL of 100-fold concentrated eluent to each 100 mL of samples and standards.

Particles from samples may lodge in the system, causing blockage. Thus, all samples are filtered before analysis.

4.0 APPARATUS AND MATERIALS

Syringes, disposable, 10-cc
Syringe filters, Nalgene, 0.20-um pore size
Volumetric glassware
Ion chromatography system, Dionex DX100 or equivalent instrument
Guard column, Dionex AG4A (for all anions except thiosulfate)
Guard column, Dionex AG3 (for thiosulfate)
Separator column, Dionex AS3 or AS4A (for all anions except thiosulfate)
Separator column, Dionex AS3A (for thiosulfate)
Fiber suppressor column, Dionex PN 035691

5.0 REAGENTS AND STANDARDS

Standard eluent: Dissolve 1.008 g sodium bicarbonate and 1.0176 g sodium carbonate in 1500 mL of DI water. Dilute to 4 L. Mix thoroughly

Thiosulfate eluent: Dissolve 1.008 g sodium bicarbonate, 1.018 g sodium carbonate, and 0.381 g p-cyanophenol in DI water and dilute to 4 L.

Acetate, formate, and oxalate eluent: Weigh out 1.9 g sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 1OH_2O$, into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Bromate eluent: Dissolve 0.80 g $Na_2B_40_7 \cdot 10H_2O$ into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Regeneration solution (0.025 N H_2SO_4):Dilute 1.4 mL of concentrated sulfuric acid to 2000 mL with DI water. Mix thoroughly.

Commercial stock standards: For fluoride (100 ppm), chloride (500 ppm), nitrate (100 ppm), phosphate (50 ppm), and sulfate (100 ppm)

Bromide stock standard, 1000 ppm: Weigh out 1.263 g reagent grade NaBr into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Iodide stock standard, 1000 ppm: Weigh out 1.308 g reagent grade KI into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Nitrite stock standard, 100 ppm: Weigh out 0.1500 g reagent grade $NaNO_2$ into a 1-L volumetric flask. Dissolve and dilute to volume with DI water. Prepare fresh daily.

Sulfite stock standard, 1000 ppm: Weigh out 1.575 g reagent grade Na_2SO_3 into a 1-L volumetric flask. Dissolve and dilute to volume with DI water. Prepare fresh daily.

Acetate stock standard, 1000 ppm: Weigh out 1.306 g NH_4CH_3COO into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Formate stock standard, 1000 ppm: Weigh out 1.409 g NH_4C00H into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Oxalate stock standard: 1000 ppm: Weigh out 1.359 g $Na_2C_2O_4$ into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

Thiosulfate stock standard, 1000 ppm: Weigh out 2.216 g $Na_2S_2O_3 \cdot 5H_2O$ into a 1-L volumetric flask. Dissolve and dilute to volume with DI water. Prepare fresh daily.

Bromate stock standard, 1000 ppm: Weigh out 1.305 g $KBrO_3$ into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

NaOH solution, 0.1 M: Weigh out 4.0 g NaOH into a 1-L volumetric flask. Dissolve and dilute to volume with DI water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are collected in plastic purple-dot (no preservatives) sample bottles. All samples are cooled to 4°C. Holding times are 28 days for fluoride, chloride, bromide, bromate and sulfate; 48 h for nitrate, nitrite, and orthophosphate; and 24 h for iodide. Thiosulfate and sulfite samples should be analyzed as soon as possible. Other anions are determined as soon as practicable.

7.0 PROCEDURE

Select the appropriate column for the determination as found in the Apparatus and Materials section and install it into the ion chromatographic system. Turn on the power to the ion chromatograph. Select the appropriate eluent for the determination as found in the Reagents and Standards section, and attach the eluent line to the eluent reservoir. Turn on the nitrogen gas supplying pressure for the sample injection system. Set the pressure limit for the system to 1900 psi. Turn on the power to the interface for the system. Turn power on to the conductivity cell.

Set the attenuation to 1024.

Set the temperature compensation to 1.8 for thiosulfate determinations and 1.7 for all other anion determinations.

Set the conductivity output range to 3 μS for thiosulfate determinations, 10 μS for organic acid anion determinations, and 30 μS for all other anion determinations.

Set the eluent flow rate to 2.3 mL/min for thiosulfate determinations, and 2.0 mL/min for other anion determinations.

Check the baseline conductivity of the cell. It should be 2-4 μS for the organic acid anion eluent, 8-12 μS for the thiosulfate eluent, 15-20 μS for the standard eluent, and 2-3 μS for the bromate eluent.

Insure pump line is connected to valve 2, and start the pump. Allow the system to stabilize approximately 20 min.

Make up a mixed standard containing the analytes of interest by adding the amounts of stock standards shown in the table below to a 100-mL volumetric flask. Dilute to volume to give a mixed standard containing the analytes of interest at the shown concentrations.

Note that acetate, formate, oxalate, thiosulfate, and bromate anions have five standards each because of their nonlinear response.

Anion	Stock Conc. (ppm)	Volume of Stock (mL)	Mixed Std. Conc. (ppm)
Fluoride	100	10	10
Chloride	500	2	10
Bromide	1000	1	10
Nitrate	100	10	10
Phosphate	50	20	10
Sulfate	100	10	10
Iodide	1000	5	50
Nitrite	100	5	5
Sulfite	1000	1	10
Acetate, Formate, and Oxalate	1000	1	10
		0.7	7
		0.5	5
		0.3	3
		0.1	1
Thiosulfate	1000	5	50
		3	30
		2	20
		1	10
		0.5	5
Bromate	1000	0.5	5
		0.4	4
		0.3	3
		0.2	2
		0.1	1

Mixed standards are made up daily.

Calibration

After the ion chromatograph is first set up and prior to any analyses, the linearity of the response of each anion is ascertained by constructing a five-point calibration curve. In addition, the effective dynamic range of the response is determined.

The integrator can be programmed to fit a quadratic equation to the data from an analyte giving a nonlinear response and will calculate sample concentrations from this equation.

After these initial calibration curves are constructed, fewer standards are necessary to provide daily calibrations. For analytes giving a linear response (initial curve ≥ 0.990 correlation coefficient), only one calibration standard is run for daily calibration, and care is taken to insure all samples fall within the previously determined linear range for that analyte. For nonlinear analytes, a minimum of three different calibration standards are run for a daily calibration to provide three points for the calibration curve.

To calibrate, inject approximately 1 mL of standard into the injection port, rinsing and filling the attached 50-uL sample loop. Press the "**Inject**" button on the interface and the "**Inject A**" button on the integrator at the same time. The run will begin. (After 15 s, turn off the Inject button on the interface.) The ion chromatogram will automatically be printed out on the chart recorder portion of the integrator. This initial injection will define retention times for each ion.

Stop the run by pressing **Inject A** on the integrator when all of the desired peaks have eluted. Input the correct program, and reinject the one mixed standard if response is linear, or at least three standards, if the response is nonlinear.

8.0 SAMPLE ANALYSIS

Soils and Sediments

Most of the analytes listed in the Scope and Application section can be extracted from soils by the procedure below and reported as "extractable" anions. Because of the instability of thiosulfate, sulfite, and iodide, this extraction procedure is not recommended for their determination in soils.

Approximately 5 g of sample is weighed out exactly and placed in a 100-mL screw-cap plastic bottle. One hundred mL of DI water is added to the sample, the bottle is capped, placed in a rotating extractor, and rotated for 2 hours. Upon removal, the extract is filtered using a syringe filter with a 0.20-um pore size filter and analyzed as a liquid sample.

Anion concentrations in soil and sediment are calculated from their extract concentrations as shown below.

$$\textit{Anion concentration, mg/kg dw} =$$

$$\frac{mg}{L}\textit{ in extract} \otimes \frac{\textit{Volume of extract (L)} \otimes 1000\ g/kg}{\textit{Sample wt. (g)} \otimes \textit{dry wt. fraction}}$$

Liquid Samples

Samples are diluted appropriately for analysis on the ion chromatograph. Just prior to analysis, samples are filtered through 0.2-μm syringe filters. Approximately 1 mL of sample is injected into the injection port, rinsing and filling the 50-uL sample loop.

Matrix spikes are analyzed to provide information on matrix effects and are analyzed at a frequency of one matrix spike and matrix spike duplicate per 20 samples or per batch, whichever is more frequent. Spikes are made to the samples to provide the concentrations shown in the table below.

Anion	Stock Conc. (ppm)	Volume of Stock (mL)	Mixed Std. Conc. (ppm)
Fluoride	100	1	1
Chloride	500	1	5
Bromide	1000	0.5	5
Nitrate	100	0.2	0.2
Phosphate	50	0.4	0.2
Sulfate	100	5	5
Iodide	1000	2	20
Nitrite	100	0.2	0.2
Sulfite	1000	0.5	5
Acetate	1000	0.5	5
Formate	1000	0.5	5
Oxalate	1000	1	10
Thiosulfate	1000	2	10
Bromate	1000	0.3	3

NOTE: Spike concentrations of 10 ppm for acetate, formate, and oxalate anions can also be used depending on the concentrations in the samples.

Blanks containing only lab reagent water are also run.

To shut down the system, the following is done. Turn off the pump and nitrogen. Set the pressure limit to 0 psi and the flow to 0 mL/min. Turn off the power to the interface, the conductivity cell, and the integrator.

Columns are stored by leaving them connected in-line in the ion chromatography system, full of carbonate eluent. Alternatively, they can be pumped full of 0.1 M NaOH solution, removed from the system, and their ends plugged.

9.0 QUALITY CONTROL/QUALITY ASSURANCE

An initial five-point calibration curve is analyzed to establish anion response linearity and establish the linear range of the method.

Anions are considered to give a linear response if a five-point calibration curve yields a correlation coefficient of ≥ 0.990 upon application of linear regression.

Anions with linear responses are calibrated daily with a single calibration standard.

Anions with nonlinear responses are calibrated daily with at least three calibration standards. Quadratic curve fitting is generally applied.

An independent calibration verification standard is analyzed immediately upon daily calibration, after every 10 samples and at the end of each run. This standard must meet control criteria for bracketed sample data to be acceptable.

Calibration blanks are analyzed after each calibration verification standard and must be less than the PQL for the anions of interest in order for the bracketed sample data to be acceptable.

A matrix spike and matrix spike duplicate are analyzed for each batch or every 20 samples, whichever is more frequent.

In addition to the above QC, for soil/sediment samples, an LCS (spiked sand) must be extracted and analyzed in duplicate for each 20 samples or each batch, whichever is more frequent. The LCS/LCS dup must meet control criteria for the extraction batch data to be acceptable.

One extraction blank is extracted and analyzed for each 20 samples, or each batch, whichever is more frequent. Concentration of anions of interest must be less than their PQLs for the extraction batch data to be acceptable.

10.0 REFERENCES

1. *The Determination of Inorganic Anions in Water by Ion Chromatography - Method 300.0*; U.S. EPA: Cincinnati, OH, August, 1991.

2. *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.